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NOTES

ON THE

CHEMICAL LECTURES

IN THE

MEDICAL DEPARTMENT OF THE UNIVERSITY
OF PENNSYLVANIA,

FOR

SECOND-YEAR STUDENTS.

PUBLISHED BY AUTHORITY OF PROF. THEO. G. WORMLEY.

BY

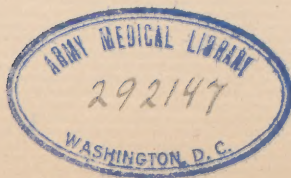
JOHN MARSHALL, M.D.,

DEMONSTRATOR OF CHEMISTRY.



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1889.



Annex

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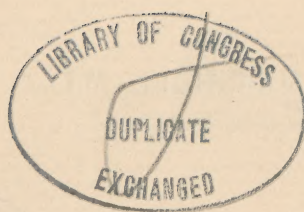
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THE following notes, by Dr. Marshall, of my Lectures on Chemistry, for students, have been published with my consent and authority.

THEODORE G. WORMLEY.

NOTES

ON

CHEMICAL LECTURES.

THE production of *organic compounds* was supposed to be due to the influence of a so-called *vital force*. This supposition was shown to be fallacious when *organic compounds* were produced artificially (by synthesis).

Liebig defined *organic chemistry* as the chemistry of the compound radicals. This definition is faulty because there are radicals, as NH_4 , SO_3 , etc., in the domain of inorganic chemistry.

The names *compound radical* and *radical* are synonymous.

A *radical* is a chemical combination of two or more elements capable of playing the part of an elementary form of matter.

Organic chemistry has been defined as the chemistry of the compounds of carbon. It must be remembered that there are two compounds containing carbon in the domain of inorganic chemistry, CO and CO_2 .

The latest definition of *organic chemistry* is,—the chemistry of the hydrocarbon compounds and their derivatives. This definition applies to all carbon compounds except HCN (hydrocyanic acid).

The number of elements entering into the composition of organic compounds is comparatively small, but the number of atoms in a molecule of a compound may be very large.

Organic compounds may be composed of simply carbon and hydrogen. Such compounds are termed hydrocarbons, as $\text{C}_{10}\text{H}_{16}$, oil of turpentine, CH_4 , methane.

Other organic compounds may be composed of three elements,—namely, carbon, hydrogen, and oxygen. Compounds of these three elements containing the hydrogen and oxygen atoms in the proportion to form water are called carbohydrates, as $\text{C}_6\text{H}_{10}\text{O}_5$, starch, $\text{C}_6\text{H}_{12}\text{O}_6$, glucose, in which there are $\text{H}_{12}\text{O}_6 = 6\text{H}_2\text{O}$.

Organic compounds may be composed of four elements,

carbon, hydrogen, oxygen, and nitrogen. Compounds containing nitrogen are termed nitrogenous or azotized, as $\text{CO}(\text{NH}_2)_2$, urea.

Some compounds are composed of only carbon and nitrogen, as CN , cyanogen, and others of carbon, nitrogen, and hydrogen, as HCN , hydrocyanic acid.

HCN , hydrocyanic acid, may be looked upon as CH_4 , methane, in which three atoms of H have been replaced by an atom of triad nitrogen, as $\text{C} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{H} \end{array}$

A few organic compounds contain carbon, hydrogen, oxygen, nitrogen, and sulphur, as $\text{C}_{204}\text{H}_{322}\text{N}_{52}\text{O}_{66}\text{S}_2$, egr-albumen. Some few contain phosphorus, as $\text{C}_{42}\text{H}_{84}\text{NPO}_9$, lecithin.

A very few organic compounds contain, in addition to carbon, hydrogen, oxygen, nitrogen, and sulphur, a *metal*,—as iron in $\text{C}_{636}\text{H}_{1025}\text{N}_{164}\text{O}_{189}\text{FeS}_3\text{O}_2$, oxyhæmoglobin. Molecular weight, 14161.

All organic compounds occurring in nature may be considered as falling under the above classification. By chemical means nearly all of the elements may be introduced into chemical compounds.

The number of possible combinations of these elements to produce new organic compounds is almost infinite. Ordinarily only fourteen or fifteen elements are concerned in organic chemistry.

Organic compounds containing sodium, copper, gold, etc., and iodine, bromine, chlorine, etc., may be produced artificially by chemical means. These compounds do not occur already formed in nature.

An *organic body* is composed of distinct organic compounds called *proximate principles*. Example, conium maculatum, an organic body, contains conine, $\text{C}_8\text{H}_{15}\text{N}$, a proximate principle. Opium, an organic body, contains many proximate principles, as morphine, $\text{C}_{17}\text{H}_{19}\text{NO}_3$, codeine, $\text{C}_{18}\text{H}_{21}\text{NO}_3$, etc. The percentage proportion of the proximate principle contained in an organic body is not definite,—i.e., two or three samples of opium selected at random will not contain, except by chance, the same percentage of morphine.

A proximate principle is a primary organic compound in which the elements are combined in definite proportions, as $\text{C}_{17}\text{H}_{19}\text{NO}_3$, morphine. The vegetable alkaloids are proximate principles.

An organic body may contain inorganic matter.

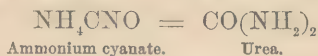
Oxygen is the predominating element in inorganic chemistry, carbon in organic chemistry.

In organic chemistry the same laws of combination apply as in inorganic chemistry.

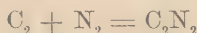
The belief that a so-called vital force was a necessity in the formation of organic compounds received its first thrust in 1828, by Woehler's synthetical production of urea from substances considered inorganic,—namely, ammonia and cyanic acid (the two forming NH_4CNO , ammonium cyanate.)



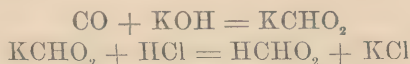
By slowly heating NH_4CNO , ammonium cyanate, on a water-bath at a temperature between 50°C. and 70°C. a rearrangement of the atoms occurs with the formation of urea.



The next organic compound produced synthetically was CN , cyanogen, by Fownes in 1841. This was produced by passing nitrogen over red-hot charcoal (carbon).



Berthelot followed in 1856 by the synthetical production of HCHO_2 , formic acid. This was produced by passing CO , carbon monoxide, over heated KOH , potassium hydroxide, forming KCHO_2 , potassium formate. The latter compound when treated with HCl (hydrochloric acid) breaks up into HCHO_2 , formic acid, and KCl , potassium chloride.



Wurtz in 1862 produced $\text{C}_2\text{H}_5\text{OH}$, ethyl alcohol, synthetically. The alkaloid coniine, $\text{C}_8\text{H}_{15}\text{N}$, has been produced synthetically.

Thousands of organic compounds have been produced synthetically in the past twenty-five years, some of them of the greatest importance; for example, the aniline coloring-matters, indigo, and many of the medicines now largely used in practice. The number of organic compounds produced synthetically is far greater than those existing in nature.

It was urged that the synthesis of urea was only the production of a simpler substance from a more complex one. $\text{K}_4\text{Fe}(\text{CN})_6$ having been the complex substance used in the

production of the NH_4CNO , ammonium cyanate, from which the urea was finally produced. This was met by the synthetical production of a complex substance, $\text{C}_{21}\text{H}_{18}\text{N}_2$, hydrobenzamide, from a more simple one, $\text{C}_7\text{H}_6\text{O}$, benzamide, oil of bitter almonds. This was effected by passing NH_3 , ammoniacal gas, into $\text{C}_7\text{H}_6\text{O}$, oil of bitter almonds.



A *radical* is a chemical combination of two or more elements capable of playing the part of an elementary form of matter.

Behaving as an element, radicals must have equivalence (valence) and electrical affinities corresponding with elements. They may be monivalent, divalent, etc., and either positive or negative. As they are unsaturated molecules a neutral radical is an impossibility.

In 1782, Scheele recognized the compound $\text{Hg}(\text{CN})_2$, mercuric cyanide, and in 1815, Gay-Lussac isolated CN , *it being the first radical isolated*.

CN or Cy may be taken as the type of the *negative* radicals. It may be compared with the negative element Cl , chlorine.

KCl , also KCN , a simple salt,—potassium cyanide.

AgCl , also AgCN , a simple salt,—argentic cyanide.

HCl , also HCN , a hydrogen acid,—hydrocyanic acid.

HClO , also HCNO , an oxyacid,—cyanic acid.

KClO , also KCNO , an oxyacid salt,—potassium cyanate.

CN therefore unites with—

1. Hydrogen to form a hydrogen acid.
2. Metals to form simple salts.
3. Hydrogen and oxygen to form an oxyacid.
4. Hydrogen, oxygen, and a metal to form an oxyacid salt.

The negative radical may contain a metal. When KCN , potassium cyanide, is heated with metallic iron in the presence of air, a new radical, called ferrocyanogen, $\text{Fe}(\text{CN})_6$, is formed.



The radical $\text{Fe}(\text{CN})_6$ has never been isolated. Sometimes it is expressed FeCy_6 or Cfy . It is a tetrad radical. The K in $\text{K}_4\text{Fe}(\text{CN})_6$ may be replaced by H , forming $\text{H}_4\text{Fe}(\text{CN})_6$, ferrocyanic acid.

If chlorine be passed through a solution of $\text{K}_4\text{Fe}(\text{CN})_6$, one

atom of K is withdrawn, and $K_3Fe(CN)_6$, potassium ferricyanide, is formed.



The negative radical $Fe(CN)_6$ is now a triad. It has never been isolated. The K in $K_3Fe(CN)_6$ may be replaced by H, forming $H_3Fe(CN)_6$, ferricyanic acid.

C_2H_5 , ethyl, may be taken as the type of the *positive* organic radicals. It may be compared with the positive element K, potassium.

KCl,	also	C_2H_5Cl ,	ethyl chloride.
K_2S ,	"	$(C_2H_5)_2S$,	ethyl sulphide.
K_2O ,	"	$(C_2H_5)_2O$,	ethyl oxide.
$KHSO_4$,	"	$C_2H_5HSO_4$,	ethyl sulphuric acid.
KCN,	"	C_2H_5CN ,	ethyl cyanide.
KCNO,	"	C_2H_5CNO ,	ethyl cyanate.

C_2H_5 therefore unites with—

1. Members of the chlorine group to form simple salts.
2. Oxygen to form an oxide.
3. An oxyacid to form an oxyacid salt.

The first positive radical containing a metal isolated was $(CH_3)_2As$, kakodyl (alkarsin, dimethylarsin). It is sometimes represented by the abbreviation Kd. It is a monad radical. It has an intense affinity for oxygen, combining with it to form $((CH_3)_2As)_2O$, kakodyl oxide, sometimes represented by Kd_2O . Kakodyl combines with chlorine to form $(CH_3)_2AsCl$, kakodyl chloride, and CN to form $(CH_3)_2AsCN$, kakodyl cyanide.

Kakodyl alone and in combination (except as kakodylic acid) is very poisonous.

Kakodyl when exposed to the air in the presence of water forms $(CH_3)_2AsOOH$, kakodylic acid, sometimes abbreviated to $HKdO_2$.

Kakodylic acid contains 54 per cent. of metallic arsenic, equivalent to 71.4 per cent. of As_2O_3 , arsenious oxide, but is not poisonous. It is the only kakodyl compound that is not poisonous.

Kakodyl may be compared with K.

KCl,	also	$(CH_3)_2AsCl$,	kakodyl chloride.
K_2O ,	"	$((CH_3)_2As)_2O$,	kakodyl oxide.
K_2SO_4 ,	"	$((CH_3)_2As)_2SO_4$,	kakodyl sulphate.

$(\text{CH}_3)_2\text{As}$, kakodyl, therefore unites with—

1. Members of the chlorine group to form simple salts.
2. Oxygen to form an oxide.
3. An oxyacid to form an oxysalt.

There are similar compounds of antimony and of zinc.

CH_4 , methane, may be considered a type of the saturated organic compounds. All of the carbon bonds are satisfied, and it is therefore a saturated molecule. One, two, three, or all four atoms of H in CH_4 may be replaced by other elements. The radical remaining after the withdrawal of each atom of hydrogen has an equivalence (valence) corresponding to the number of hydrogen atoms withdrawn.

1. $\text{CH}_4 - \text{H} = \text{CH}_3$ (methyl), univalent.
2. $\text{CH}_4 - \text{H}_2 = \text{CH}_2$ (methene), bivalent.
3. $\text{CH}_4 - \text{H}_3 = \text{CH}$ (formyl), trivalent.
4. $\text{CH}_4 - \text{H}_4 = \text{C}$ (carbon), quadrivalent.

Thus replacing the H by Cl we have—

1. $\text{CH}_4 + 2\text{Cl} = \text{CH}_3\text{Cl} + \text{HCl}$.
2. $\text{CH}_4 + 4\text{Cl} = \text{CH}_2\text{Cl}_2 + 2\text{HCl}$.
3. $\text{CH}_4 + 6\text{Cl} = \text{CHCl}_3$ (chloroform) + 3HCl .
4. $\text{CH}_4 + 8\text{Cl} = \text{CCl}_4 + 4\text{HCl}$.

Or replacing the H by iodine we have—

1. $\text{CH}_4 + 2\text{I} = \text{CH}_3\text{I} + \text{HI}$.
2. $\text{CH}_4 + 4\text{I} = \text{CH}_2\text{I}_2 + 2\text{HI}$.
3. $\text{CH}_4 + 6\text{I} = \text{CHI}_3$ (iodoform) + 3HI .
4. $\text{CH}_4 + 8\text{I} = \text{CI}_4 + 4\text{HI}$.

A *type* is a form of chemical combination common to a class of compounds.

NaCl , type of simple salts.

K_2SO_4 , “ oxysalts.

H_2O , the water type.

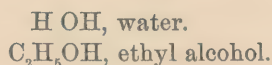
NH_3 , “ ammonia type.

By *substitution* we mean the replacing of one or more elements or radicals in a compound by one or more elements or radicals without changing the type of the compound.

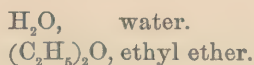
When chemical combination occurs it does not necessarily follow that substitution has taken place.

Alcohols and ethers may be viewed as substitution compounds.

An alcohol may be considered after the type of water, in which *one* atom of H in H_2O has been replaced by an alcohol radical, as



An ether may be considered after the type of water, in which *both* atoms of H in H_2O have been replaced by alcohol radicals, as



EXAMPLES OF SUBSTITUTION. ,

When $HgCl_2$, *mercuric chloride*, is treated with NH_3 , ammoniacal gas, one of the atoms of Cl in the $HgCl_2$ is replaced by the amido-radical NH_2 , and $HgNH_2Cl$, *amido-mercuric chloride* (white precipitate), is formed.

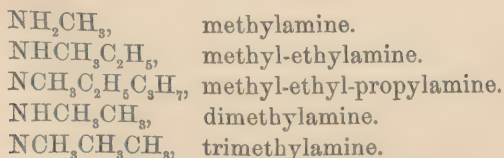


When Hg_2Cl_2 , *mercurous chloride*, is treated with NH_3 , ammonia, one of the atoms of Cl in the Hg_2Cl_2 is replaced by the amido radical NH_2 , and Hg_2NH_2Cl , *amido-mercurous chloride* (black precipitate), is formed.



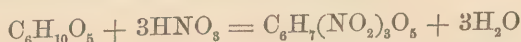
One, two, or all three atoms of H in NH_3 may be replaced by other elements or radicals.

We may have NH_2K , potass-amine, produced by the replacement of one atom of H in NH_3 by K. By the replacement of H in NH_3 by radicals we may have

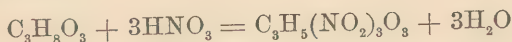


All the atoms of hydrogen in a compound are not necessarily replaceable. For example, only one atom of hydrogen in $HC_2H_3O_2$, acetic acid, is replaceable.

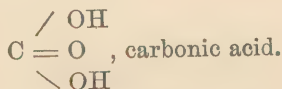
When $C_6H_{10}O_5$, *cellulose* (cotton), is treated with nitric acid, three atoms of hydrogen in the cellulose are replaced by the NO_2 , nitro radical, forming the explosive compound $C_6H_7(NO_2)_3O_5$, *trinitrocellulose* (gun-cotton).



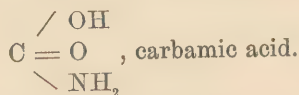
When $C_3H_8O_3$, *glycerine*, is treated with nitric acid, three atoms of hydrogen in the glycerine are replaced by the NO_2 , nitro radical, forming the explosive compound $C_3H_5(NO_2)_3O_3$, *trinitroglycerine*.



The hypothetical H_2CO_3 , carbonic acid, is dibasic; has two replaceable atoms of hydrogen.



By replacing one of the OH hydroxyl groups in carbonic acid by NH_2 , an amido-acid, carbamic acid is obtained.

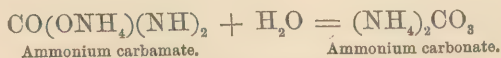


Carbamic acid is not known in its free state. It is always in combination as a salt or an ether. The ammonium salt is produced by bringing together dry CO_2 , carbon dioxide, and dry NH_3 , ammoniacal gas.

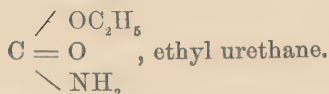
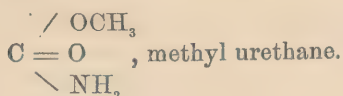
$CO_2 + 2NH_3 = CO(OH)(NH_2)$ or $NH_4NH_2CO_2$, ammonium carbamate.



When treated with water it decomposes into ammonium carbonate.

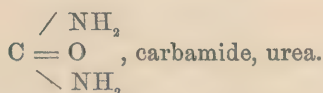


The ethers of carbamic acid are called *urethanes*. They are formed by replacing the atom of hydrogen in the remaining OH hydroxyl group in $CONH_2OH$, carbamic acid, by an alcohol radical.



Ethyl urethane under the name of "*urethane*" is now used in medicine.

By replacing both of the hydroxyl groups in H_2CO_3 , carbonic acid, by NH_2 , an amide is formed, $\text{CO}(\text{NH}_2)_2$, carbamide, urea.



Antipyrin, $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2$, or $\text{C}_{18}\text{H}_{12}(\text{CH}_3)_2\text{O}_2\text{N}_4$, dimethyloxy chinizin, is a substitution product.

The aniline coloring-matters are also substitution products.

The composition of organic compounds may be expressed by—

1. Empirical formula.
2. Molecular formula.
3. Rational formula.
4. Graphic formula.

1. *Empirical formula*: The simplest possible expression by formula of the composition of a compound. It simply indicates the elements that enter into the composition of the compound in their least atomic proportions. Thus CH_2O for acetic acid.

An empirical formula may be deduced from the results of a quantitative analysis of a compound.

2. *Molecular formula*: A formula that expresses a quantity of a compound twice its specific gravity in the gaseous state compared with hydrogen.

Or: A quantity of a compound in the gaseous state twice the volume of the atom of hydrogen. Hence all molecules must be of the same size.

A molecular formula may be determined:

a. By determining the specific gravity of the compound in the gaseous state.

Victor Meyer's method: Depends on the vaporization of a weighed quantity of a compound and measuring, by means of

a eudiometer, the volume of air the vapor displaces in the apparatus, correcting for temperature and pressure, and comparing the volume of air displaced with the volume occupied by a quantity of hydrogen equal to the weight of the compound volatilized.

The molecular weight of a compound which undergoes decomposition before its point of vaporization is reached cannot be determined by this method.

Method: A substance having a fixed boiling-point is placed in the outer large glass tube. For compounds having a low vaporizing-point water may be used. Generally $(C_6H_5)_2NH$, diphenylamine, having a boiling-point of $310^\circ C.$, is employed. Melted lead may be used for compounds having a higher vaporizing-point. The smaller bulbed glass tube having a curved delivery-tube attached is lowered into the larger glass tube until the bulbed end is a few inches above the surface of the substance having a fixed boiling-point. A small quantity of the compound, of which the molecular weight is to be determined, is weighed off in a very small glass tube, which is closed at one end. The tube containing the compound is placed with the opening upward in a perforation in the cork of the smaller bulbed tube, where it is held in place by a wire thumb-screw contrivance, and the cork thus arranged placed in the smaller bulbed tube. Gentle heat is applied to the outer large tube, and gradually increased until the substance with the fixed boiling-point boils. After boiling a few minutes and the vapor of the boiling material reaches and is condensed to a liquid at a point opposite the bulb of the smaller glass tube, the delivery-tube is adjusted so that the exit is below the surface of water contained in a suitable vessel. When bubbles of air cease to ascend through the water (the heating of the material at the same time being kept up so that it is boiling), a eudiometer filled with water is inverted over the exit of the delivery-tube under water, and by turning the thumb-screw contrivance the tube containing the compound under examination is allowed to drop to the bottom of the inner bulbed tube. (To break the fall of the tube containing the compound it is customary to previously place pieces of broken glass tubing in the bottom of the bulb of the inner glass tube.)

Volatilization of the compound immediately occurs, and a volume of air is displaced and collected in the eudiometer exactly equivalent to the gaseous volume furnished by the

weight of the compound volatilized. This final part of the operation requires but a few minutes.

When bubbles of air cease to come over, the cork is taken out of the apparatus and the eudiometer cautiously removed and placed in a vessel containing water. After a time the air in the eudiometer becomes of the same temperature as the water surrounding it. The volume of air is now read off, the temperature of the water surrounding the eudiometer and the barometric pressure are observed, and the necessary calculations performed.

Suppose 0.010 acetic acid were volatilized and the volume of air displaced and collected in the eudiometer, corrected for temperature (0° C.) and barometric pressure (760 mm.), measured 3.72 c.c.

0.010 hydrogen at 0° C. temperature and 760 mm. pressure measure 111.6 c.c.

$$\text{Then } 111.6 \div 3.72 = 30$$

showing the vapor of acetic acid to be 30 times more dense, volume for volume, than hydrogen.

$$\text{Or } 11160 \text{ c.c.} : 1 \text{ gram. H} :: 3.72 : 0.0003$$

All molecules, elementary or compound, must be equal in volume to the volume occupied by the molecule of hydrogen,—*i.e.*, twice the atomic volume.

If 30 grammes of acetic acid in the form of vapor will occupy the same volume as the atomic volume of hydrogen,—namely, 11160 c.c.,—then 60 grammes of acetic acid will occupy twice the atomic volume, or the molecular volume of hydrogen,—namely, 22320 c.c.

A formula for acetic acid representing 30 as its molecular weight would be $\text{CH}_2\text{O} = 30$, really its empirical formula, and expresses a quantity in the gaseous state equal to the specific gravity of hydrogen. By multiplying the 30 by 2 = 60, we have a number representing its molecular weight. A formula for the acid constructed to represent this number would be $\text{C}_2\text{H}_4\text{O}_2 = 60$,—*i.e.*, a formula that expresses a quantity of the compound twice its specific gravity in the gaseous state compared with hydrogen.

b. The molecular weight of an organic compound, especially those compounds which are not vaporizable, may be determined,—

1. If an acid, by combining it with a metal to form a salt and determining the quantity of the metal in combination in a given quantity of the salt.

2. If a basic substance, by combining it with an acid and determining the quantity of acid in combination in a given quantity of the salt.

The molecular formula of many compounds which will not vaporize or form salts is determined by analyzing their substitution products.

The molecular formula of some compounds which will not vaporize, form salts or substitution products, is not definitely known, as cane-sugar, starch.

For example, the molecular formula of acetic acid, which forms a salt with silver, may be determined by estimating the quantity of metallic silver in its silver salt.

Suppose 1.0 gramme of argentic acetate be placed in a crucible and heated until all the organic matter is driven off and nothing remains but metallic silver. After cooling, the silver is weighed.

Quantity of argentic acetate taken	1.0000	gram.
Weight of resulting metallic silver	0.6468	"
<hr/>			
Quantity of organic compound C, H, and O; which			
must have been in combination with the silver		0.3532	"
Then			

At. wt. of silver.

$0.6468 : 0.3532 :: 108 : 58.98 = \text{C, H, and O, in combination with one atom of silver.}$

Acetic acid is a monobasic acid,—i.e., having one replaceable atom of hydrogen. Consequently, as silver is a monad, it would take the place of one atom of hydrogen in the molecule of acid. Add 1 to 58.98 = 59.98, and allowing for error in analysis, call it 60.0. A formula constructed to equal that number would be $\text{C}_2\text{H}_4\text{O}_2 = 60$, acetic acid.

The formula of the silver salt is $\text{AgC}_2\text{H}_3\text{O}_2$.

A recent method for determining molecular weight is based upon the observations of Raoult (1883),—namely, that the *lowering of the freezing-point* of a solution is proportional to the absolute quantity of substance in solution and *inversely* as its molecular weight.

3. A *rational formula* attempts to express the arrangement of the atoms or groups of atoms in the molecule of a compound.

The same compound may be represented by various rational formulas, depending on the views of different chemists,—*e.g.*, over twenty rational formulas have been suggested for acetic acid.

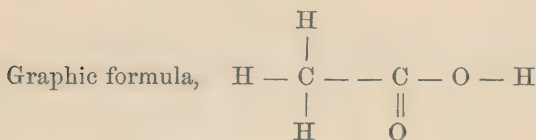
4. A *graphic formula* attempts to express the arrangement of the atoms or groups of atoms in the molecule of a compound by means of lines (pictures).

Acetic acid.

Empirical formula, CH_2O

Molecular “ $\text{C}_2\text{H}_4\text{O}_2$

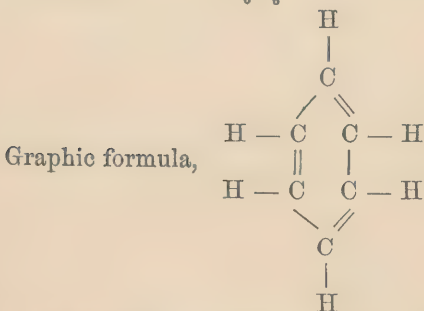
Rational “ $\text{HC}_2\text{H}_3\text{O}_2$ or CH_3COOH



Benzol (benzene).

Empirical formula, CH

Molecular “ C_6H_6



All of the atoms of hydrogen in benzol are replaceable.

By replacing the hydrogen atoms in benzol with chlorine we may have

$\text{C}_6\text{H}_5\text{Cl}$, monochlor.	benzol.
$\text{C}_6\text{H}_4\text{Cl}_2$, dichlor.	“
$\text{C}_6\text{H}_3\text{Cl}_3$, trichlor.	“
$\text{C}_6\text{H}_2\text{Cl}_4$, tetrachlor.	“
C_6HCl_5 , pentachlor.	“
CCl_6 , hexa- or perchlor.	“

Amido-benzol, or aniline, $\text{C}_6\text{H}_5\text{NH}_2$, is a compound formed by replacing one of the atoms of hydrogen in benzol by the NH_2 , amido group.

Phenol, or *carbolic acid*, C_6H_5OH , may be produced by replacing one of the hydrogen atoms in benzol by the OH hydroxyl group.

Phenol is eliminated in the urine as $C_6H_5HSO_4$, phenol-sulphuric acid, or in combination as a salt, $C_6H_5KSO_4$, phenol-potassium sulphate. Phenol (carbolic acid) is poisonous, but the salts of phenol-sulphuric acid are not poisonous. Sodium sulphate, or magnesium sulphate is recommended as an antidote in carbolic acid poisoning, converting the acid into the non-poisonous salt phenol-sodium sulphate, or phenol-magnesium sulphate.

Precipitation of barium as barium sulphate does not occur on the addition of barium chloride to a solution of the salts of phenol-sulphuric acid. Thus, from the amount of precipitate of barium sulphate obtained on the addition of barium chloride to the urine, after the ingestion of carbolic acid, it appears that the quantity of sulphuric acid is diminished, whereas it really is unchanged or perhaps increased.

Isomerism is a term applied to bodies containing the same elements united in the same relative proportions by weight, but differing more or less widely in their physical, physiological, and chemical properties.

Isomeric Compounds are of Two Classes.—1. *Polymeric*: where the *percentage* composition is similar, but the *molecular* composition dissimilar,—i.e., the same empirical but different molecular formula.

The olefines are examples of polymeric compounds, as are also the cyanogen oxyacids.

$HCNO$, cyanic acid, monobasic.

$H_2C_2N_2O_2$, fulminic acid, bibasic.

$H_3C_3N_3O_3$, fulminuric acid, monobasic.

$H_3C_3N_3O_3$, cyanuric acid, tribasic.

2. *Metameric*: Where both the percentage and the molecular compositions are alike.

The oils of turpentine, lemons, bergamot, cloves, and pepper are examples of metameric compounds. They all have a similar percentage and molecular composition, $C_{10}H_{16}$.

$C_3H_6O_3$, lactic acid,
 $C_3H_6O_3$, paralactic acid,
 $C_3H_6O_3$, hydracrylic acid,

} are metameric.

An *homologous series* is a series of chemical compounds made up of the same elements, but having a common difference in their molecular composition.

Hydrocarbons of equal equivalence, as CH_4 , may exist separately, whilst hydrocarbons of unequal equivalence, as CH_3 , are incapable of existing in the free state, unless, perhaps,

CH_3
as double molecules,—i.e., $|\text{CH}_3 = \text{C}_2\text{H}_6$.
 CH_3

As examples of homologous series we have the—

1. Olefines.
2. Alcohol radicals.
3. Paraffins.
4. Alcohols.
5. Aldehydes.
6. Volatile fatty acids.
7. Ethers.

1. *Olefines*: Diatomic, polymeric, hydrocarbon compounds.

		Vapor density compared with H.	
1.	CH_{27} , methene (hypothetical)	.	7
2.	C_2H_4 , ethene	14
3.	C_3H_6 , propene	21
4.	C_4H_8 , butene	28
5.	C_5H_{10} , pentene	35
6.	C_6H_{12} , hexene	42
7.	C_7H_{14} , heptene	49
8.	C_8H_{16} , octene	56
9.	C_9H_{18} , nonene	63
10.	$\text{C}_{10}\text{H}_{20}$, decene	70

30. $\text{C}_{30}\text{H}_{60}$, melene, found in wax.

2. *Alcohol radicals*, (may only exist as double molecules):

Olefines + one atom of H, hydrides of the olefines, monatomic.

1. CH_3 , methyl.
2. C_2H_5 , ethyl.
3. C_3H_7 , propyl.
4. C_4H_9 , butyl.
5. C_5H_{11} , amyl.
- Etc.

The alcohol radicals form salts, as CH_3I , CH_3Cl , etc.

3. *Paraffins*: Alcohol radicals + one atom of H, hydrides of the alcohol radicals, saturated hydrocarbons.

1. CH_4 , methane.
2. C_2H_6 , ethane.
3. C_3H_8 , propane.
4. C_4H_{10} , butane or quartane.
5. C_5H_{12} , pentane.
6. C_6H_{14} , hexane.

4. *Alcohols*, monatomic or monohydric, ethylic series: Alcohol radicals + OH (hydroxyl), may be regarded after the type of H_2O , in which one atom of H in H_2O has been replaced by an alcohol radical.

	Vapor density compared with H.	Boiling- point.
1. CH_3OH , methylic alcohol (wood spirit)	. 16	150° F.
2. $\text{C}_2\text{H}_5\text{OH}$, ethylic " (ordinary alcohol).	. 23	173°
3. $\text{C}_3\text{H}_7\text{OH}$, propylic " 30	205°
4. $\text{C}_4\text{H}_9\text{OH}$, butylic " 37	233°
5. $\text{C}_5\text{H}_{11}\text{OH}$, amylic " 44	270°
6. $\text{C}_6\text{H}_{13}\text{OH}$, caprylic " 51	305°
Etc.		

5. *Aldehydes* of the acetic series, (alcohol dehydrogenatum): Alcohols minus two atoms of H. Under the influence of oxidizing agents alcohols give up two atoms of H, forming aldehydes,—viz., $\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{O} + \text{H}_2\text{O}$.

1. CH_2O , methylic or formic aldehyde.
2. $\text{C}_2\text{H}_4\text{O}$, ethylic or acetic "
3. $\text{C}_3\text{H}_6\text{O}$, propylic "
4. $\text{C}_4\text{H}_8\text{O}$, butylic "
5. $\text{C}_5\text{H}_{10}\text{O}$, valeric "
- Etc.

6. *Fat acids*, acetic series: Aldehydes + one atom of oxygen, monatomic.

1. CH_2O_2 , formic acid, found in red ants.
2. $\text{C}_2\text{H}_4\text{O}_2$, acetic " " " vinegar.
3. $\text{C}_3\text{H}_6\text{O}_2$, propylic " " " oils.
4. $\text{C}_4\text{H}_8\text{O}_2$, butyric " " " rancid butter.
5. $\text{C}_5\text{H}_{10}\text{O}_2$, valeric " " " valerian.
6. $\text{C}_6\text{H}_{12}\text{O}_2$, caproic " " " rancid butter and sweat.

And continuing regularly to

20. $C_{20}H_{40}O_2$, butic acid, found in butter.

30. $C_{30}H_{60}O_2$, melissic " " " beeswax.

7. *Ethers*, of *monohydric alcohols*: Oxides of the alcohol radicals, after the type of H_2O , in which both atoms of H in the H_2O are replaced by alcohol radicals.

1. $(CH_3)_2O$, methylic ether.

2. $(C_2H_5)_2O$, ethylic "

3. $(C_3H_7)_2O$.

4. $(C_4H_9)_2O$, butylic "

5. $(C_5H_{11})_2O$, amyllic "

Every alcohol has its corresponding aldehyde, acid, and ether.

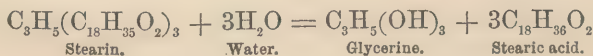
The *paraffins* are saturated hydrocarbon compounds.

By replacing 3 atoms of H in a paraffin with 3 hydroxyl (OH) groups a triatomic (trihydric) alcohol is formed. Glycerine ($C_3H_5(OH)_3$) is a triatomic alcohol.

Replacing 3 atoms of H in the paraffin C_3H_8 , propane, with
 $\begin{array}{c} OH \\ OH \\ OH \end{array}$
 3 hydroxyl groups, a triatomic alcohol, $C_3H_5OH = C_3H_8O_3$,
 $\begin{array}{c} OH \\ OH \\ OH \end{array}$
 glycerine (propenyl alcohol), is formed.

Glycerine occurs in most animal and vegetable fats in combination with the acids of the acetic and oleic series,—as glycerides. Suet contains stearin, $C_3H_5(C_{18}H_{35}O_2)_3$, a glyceride of stearic acid.

By the action of superheated steam on the stearin in fats glycerine and stearic acid are set free.



All the monatomic alcohols of the ethylic series (the ordinary alcohols) excepting the first two members of the series have numerous isomeric modifications. They are distinguished especially by their behavior on oxidation. Kolbe gave to methylic alcohol, CH_3OH , the name carbinol, whilst all the succeeding alcohols of the series he termed carbinols, regarding them as derivatives of the first term CH_3OH , methylic alcohol, and formed by the replacement of hydrogen by monad alcohol radicals.

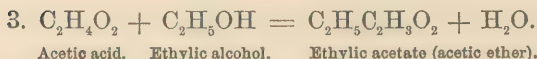
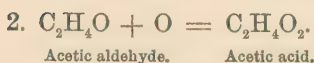
1. *Primary alcohols*: Compounds in which one atom of H of the CH_3 of carbinol (CH_3OH) is replaced by an alcohol radical.

a. $\text{CH}_2\text{CH}_3\text{OH} = \text{C}_2\text{H}_5\text{OH}$, methyl carbinol (ethyl alcohol).

b. $\text{CH}_2\text{C}_2\text{H}_5\text{OH} = \text{C}_3\text{H}_7\text{OH}$, ethyl carbinol (propyl alcohol).

Primary alcohols on oxidation yield—

1. An aldehyde.
2. A monobasic acid.
3. An ethereal salt.



2. *Secondary alcohols*: Compounds in which two atoms of H of the CH_3 of carbinol are replaced by alcohol radicals.

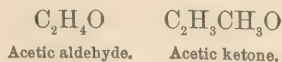
a. $\text{CHCH}_3\text{CH}_3\text{OH} = \text{C}_3\text{H}_7\text{OH}$, dimethyl carbinol (propyl alcohol).

b. $\text{CHCH}_3\text{C}_2\text{H}_5\text{OH} = \text{C}_4\text{H}_9\text{OH}$, ethyl methyl carbinol (butyl alcohol).

Secondary alcohols on oxidation yield—

1. No aldehyde.
2. A ketone.
3. An acid containing a less number of carbon atoms than the alcohol oxidized,—i.e., an acid of the fat series.

Ketone: An aldehyde in which one atom of hydrogen is replaced by an alcohol radical.



3. *Tertiary alcohols*: Compounds in which three atoms of H in the CH_3 of carbinol are replaced by alcohol radicals.

a. $\text{CCH}_3\text{CH}_3\text{CH}_3\text{OH} = \text{C}_4\text{H}_9\text{OH}$, trimethyl carbinol (pro-

pylic alcohol), $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{OH} = \text{C}_4\text{H}_9\text{OH}$, trimethyl carbinol
 (propylic alcohol).

b. $\text{CCH}_3\text{CH}_3\text{C}_2\text{H}_5\text{OH} = \text{C}_5\text{H}_{11}\text{OH}$, ethyl dimethyl carbinol
 (amylic alcohol).

Tertiary alcohols on oxidation yield—

1. No aldehyde.
2. No ketone.
3. One or more acids of the acetic series.

Four primary alcohols;
 Three secondary alcohols;
 One tertiary alcohol;

are possible, having the same empirical and molecular formula. Six of these are well known, the other two have not yet been discovered.

DECOMPOSITION OF ORGANIC SUBSTANCES.

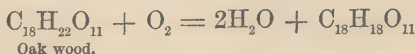
All organic substances are naturally prone to undergo decomposition. If the organic substance contain nitrogen, the tendency towards decomposition is increased.

DECOMPOSING AGENTS.

1. Oxygen.

1. *Direct combustion.*

2. *Slow combustion* as in the eremacausis (slow oxidation) of oak wood.



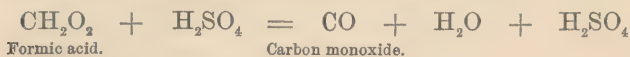
then



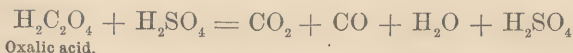
i.e.,—as soon as two atoms of oxygen have taken away four atoms of hydrogen, one atom of carbon unites with two atoms of oxygen, and so on until finally nothing remains of the oak wood but carbon. This is sometimes used as an illustration of the formation of coal.

3. *When nitrogen* is present in the compound, fermentation or putrefaction may take place. Ammoniacal gas, NH_3 , may be given off.

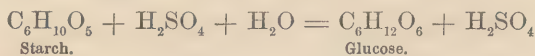
b. It may decompose the organic compound, as



c. It may abstract the elements of water from the organic compound, as



d. It may introduce the elements of water into the organic compound (assimilate the elements of water), as



The property of H_2SO_4 converting starch into glucose is made use of in estimating starch quantitatively,—*i.e.*, converting the starch into glucose and determining the quantity of the latter, and calculating the amount of starch from the amount of glucose obtained.

$\text{C}_6\text{H}_5\text{OH}$, phenol (carbolic acid), treated with H_2SO_4 forms $\text{C}_6\text{H}_5\text{HSO}_4$, phenol sulphuric acid.

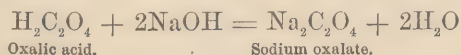


This acid ($\text{C}_6\text{H}_5\text{HSO}_4$) is formed when carbolic acid is ingested.

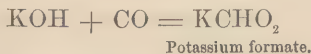
The salts of phenol sulphuric acid are not poisonous. Antidote for carbolic acid, sodium sulphate, or any soluble non-poisonous sulphate.

4. Alkalies.

a. If the organic compound be an acid, alkalies will combine with it and form salts, as



b. Alkalies may cause combination of the elements in a compound.



c. If the compound acted upon by the alkali contain nitrogen directly combined, the nascent hydrogen evolved in the decomposition combines with the nitrogen to form NH_3 , ammonia.

The alkaline substance usually employed is soda-lime, composed of

One part NaOH (caustic soda).
Two parts CaO (caustic lime).

PUTREFACTION AND FERMENTATION.

Putrefaction: Chemical decomposition of nitrogenous organic compounds, under certain conditions, by bacteria, with the evolution of more or less unpleasant odors.

Prof. Sir Henry Roscoe, F.R.S., says, in connection with the causation of the symptoms in infectious diseases, that "the symptoms of infectious diseases are no more due to the microbes which constitute the infection than alcoholic intoxication is produced by the yeast-cell, but these symptoms are due to the presence of definite chemical compounds, the result of the life of these microscopic organisms."

Fermentation: Decomposition of certain non-nitrogenous organic compounds in the presence of certain nitrogenized substances known as fermentation fungi.

Ferment: A nitrogenous body capable of inducing fermentation in a non-nitrogenous body. Yeast-cell is an example of a ferment.

Ordinary yeast is composed principally of two varieties of cells,—

Torula cerevisiæ (large round cells).

Penicilium glaucum (small oval cells).

Fermentescible body: A non-nitrogenous body capable of undergoing fermentation. Glucose is an example of a fermentescible body.

Amygdaline, a fermentescible body, is broken up by *emulsine*, a ferment (both being constituents of bitter almonds, peach-kernels, etc.), into



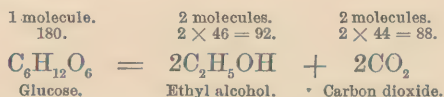
Certain conditions are necessary in a fermentation,—viz., the presence of a ferment, a fermentescible body, and moisture, a certain temperature, 20° to 40° C. (70° to 100° F.). Air must be present, at least at the beginning of the fermentation. The presence of a small quantity of salts of the alkaline earths facilitates the progress of fermentation.

Fermentation may be prevented by metallic salts, as HgCl_2 , CuSO_4 , etc., a temperature above 100° F. and below 70° F.

There are five varieties of fermentation, their distinctive names being derived from the principal product furnished:

- | | |
|---|------------|
| 1. Alcoholic, or vinous, in which alcohol | is formed. |
| 2. Acetous, " " acetic acid | " " |
| 3. Lactic, " " lactic acid | " " |
| 4. Butyric, " " butyric acid | " " |
| 5. Viscous, " " a gummy matter | " " |

1. *Alcoholic fermentation* is fermentation characterized by the formation of alcohol. It results from the action of yeast on a solution of glucose. The active agent or *ferment* is the *torula cerevisiæ* of the yeast. Ninety-five per cent. of the glucose is fermented.



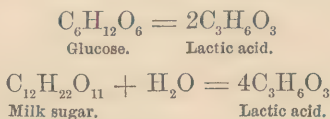
Advantage is taken of this action to estimate the quantity of glucose in urine.

When the alcohol in the solution reaches 20 per cent., fermentation ceases. A solution containing 25 per cent. of glucose will not undergo fermentation.

2. *Acetous fermentation* is fermentation characterized by the formation of acetic acid. It is an advanced stage of the alcoholic fermentation. The active agent or *ferment* is the *mycoderma aceti*. It appears to act as a carrier of oxygen.

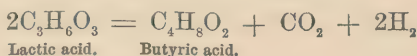


3. *Lactic acid fermentation* is fermentation characterized by the formation of lactic acid. It results from the action of putrefying cheese or milk on glucose or milk sugar. The active agent or *ferment* is the *penicilium glaucum*.



Milk sugar and *lactose* are not the same compounds. Lactose is derived from milk sugar and has the formula $C_6H_{12}O_6$.

4. *Butyric acid fermentation* is fermentation characterized by the formation of butyric acid. It is an advanced stage of the lactic acid fermentation. The *ferment* is the *penicilium glaucum*, same as in lactic acid fermentation.



5. *Viscous fermentation* is a fermentation characterized by the formation of gummy matters. It occurs in fermenting the juice of the sugar-beet, and also in sweet white wines, the liquid becoming "ropy." It may be arrested by the addition of a little alum or calcium sulphate. It does not occur in red wines because of the presence of astringent substances. The particular *ferment* causing this fermentation is *unknown*.

ORGANIC ANALYSIS.

PROXIMATE AND ULTIMATE.

Proximate Analysis.—The separation and estimation of the organic compounds contained in an organic body, as the separation of morphine, etc., from opium.

Ultimate Analysis.—The detection and estimation of the ultimate elements entering into the composition of an organic compound, as the quantity of C, H, O, and N in morphine.

That the compound is organic may be shown by heating it on platinum foil; if it chars it is organic. Some compounds volatilize before the temperature of the charring-point is reached, and others undergo decomposition without charring. Such compounds must be heated in a sealed glass tube or with cupric oxide. If CO_2 or H_2O are given off when the compound is heated with cupric oxide, it is organic.

Organic compounds may be composed of C and H or C and N; C, H, and O; C, H, N, and O; C, H, N, O, and S; C, H, N, O, S, and P.

Compounds artificially prepared may contain Cl, Br, I, As, Sb, etc.

QUALITATIVE ANALYSIS.

Presence of C and H.—Shown by the compound charring when heated alone, or producing CO_2 and H_2O when heated with cupric oxide.

Presence of Nitrogen.—*a*. Many compounds containing nitrogen, when burned, evolve an odor similar to that of burnt feathers.

b. Many compounds containing nitrogen, when heated with an alkali or with soda-lime, give rise to the formation of ammoniacal gas (NH_3), which may be detected by its odor, and, when in solution, by its forming a precipitate of $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$ on the addition of platinic chloride.

c. To detect nitrogen in other compounds, they must be

heated with a small piece of metallic potassium or sodium, thereby forming cyanogen, which combines with potassium or sodium as a cyanide, then test for a cyanide with $\text{FeSO}_4 + \text{Fe}_2\text{Cl}_6 + \text{HCl}$,—formation of prussian blue.

Presence of Sulphur.—*a.* If the compound be a solid, heat it with a mixture of solid potassium hydroxide (KOH) (twelve parts) and solid potassium nitrate (KNO_3) (six parts): the sulphur is oxidized to sulphuric acid (in combination as K_2SO_4). Dissolve the fused mass and test with barium chloride for a sulphate.

b. If the compound be a liquid, boil it with nitric acid alone or with potassium chlorate: the sulphur is oxidized to sulphuric acid. Test for a sulphate.

If the compound be a volatile liquid, heat it in a sealed glass tube with about twenty to thirty times its volume of nitric acid and test for a sulphate.

c. To determine if the sulphur in the compound is *directly* (unoxidized) or *indirectly* (oxidized) combined with the carbon, heat it with a solution of potassium hydroxide (KOH). If the sulphur is *directly* combined, a sulphide (K_2S) will be formed. Test the solution for a sulphide with lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, black lead sulphide (PbS) will be formed, or test for a sulphide with sodium nitroprusside ($\text{Na}_2\text{NOFe}(\text{CN})_6$), producing an intense purple-red color. If the sulphur is *indirectly* combined, the solution will not respond to the tests for a sulphide, but in some cases may respond to the tests for a sulphate.

Presence of Phosphorus.—*a.* Fuse the substance with the mixture of KOH and KNO_3 , or boil it with nitric acid, as in the case of sulphur, and test the aqueous solution with ammonium chloride, ammonium hydroxide, and magnesium sulphate (magnesium mixture) for a phosphate (formation of a crystalline precipitate of MgNH_4PO_4).

b. If the organic compound be a volatile liquid, heat it in a sealed glass tube with about twenty to thirty times its volume of nitric acid and test for a phosphate.

Presence of Inorganic Matter.—*a.* Heat the substance on platinum foil, thereby burning off the organic matter, and leaving the inorganic matter as a fixed residue.

Presence of Chlorine, Iodine, or Bromine.—*a.* Mix the organic compound with caustic lime (CaO), and heat it in a combustion-tube, suspend the mixture, which was heated, in water,

slightly acidulate with nitric acid, filter, and test the filtrate with argentic nitrate for a chloride.

QUANTITATIVE ORGANIC ANALYSIS.

Ultimate or elementary analysis:

Carbon is estimated as CO_2 .

Nitrogen " " NH_3 or as N.

Sulphur " " SO_3 ($\text{BaSO}_4 = \text{S}$).²³³

Phosphorus " " P_2O_5 ($\text{Mg}_2\text{P}_2\text{O}_7 = \text{P}_2$).^{222 62}

Oxygen is estimated by difference,—i.e., after the percentages of the elements in the compound have been determined the percentages are added together, and if the result does not foot up 100, the difference between the footing and 100 is ascribed to oxygen.

Conditions to be observed in Ultimate Analysis.—1. The compound to be analyzed must be pure and dry. A crystalline substance may be purified by repeated recrystallizations. The compound may be dried by allowing it to remain some time over sulphuric acid or calcium chloride in a desiccator, or it may be dried in a hot-water or air oven. When two weighings agree with each other,—i.e., the compound ceases to lose weight,—it is considered dry.

2. The compound must be completely burned.

3. The products of the combustion must be accurately collected and weighed or measured.

Requisites for an Elementary Analysis.—1. A combustion-tube of difficultly fusible Bohemian glass, about eighteen inches in length and drawn out at one end in a bayonet-like form and sealed.

2. A combustion-furnace.

3. Geissler's or Liebig's bulbs containing a strong solution of potassium hydroxide to absorb the CO_2 formed in the combustion.

4. A U-shaped tube containing calcium chloride to absorb the H_2O formed in the combustion.

5. Cupric oxide (CuO) or fused granular lead chromate (PbCrO_4) to furnish oxygen during the progress of the combustion.

6. An aspirator.

7. A gas-holder containing air or oxygen.

Method : Estimation of Carbon and Hydrogen.—A Bohemian glass combustion-tube is about half filled with freshly heated, perfectly dry, granular cupric oxide (or lead chromate). The accurately weighed organic compound to be analyzed is placed in the tube on top of the cupric oxide, some fine cupric oxide added, and the compound thoroughly mixed with the cupric oxide by means of a copper wire terminating in a spiral. The tube is then filled to within about an inch of the end with more granular cupric oxide, placed on the combustion-furnace, and a previously weighed tube, containing calcium chloride in small pieces to absorb the H_2O produced in the combustion, is attached to it by means of a closely-fitting perforated cork. Previously weighed Geissler's or Liebig's bulbs containing a solution of KOH (specific gravity 1.27) to absorb the CO_2 formed in the combustion, and having a tube attached containing small pieces of KOH (previously weighed with the Geissler's bulbs) to absorb the last traces of CO_2 , and also to hold any moisture that might be carried over from the KOH solution in the bulbs by the current of gas, are attached to the calcium chloride tube.

The combustion-tube is heated first at the end to which the calcium chloride tube is attached; when the cupric oxide in this part of the tube is of a dull red heat the heating is commenced at the other end of the tube, and continued until the cupric oxide in that part is also of a dull red heat. The heat is then gradually extended to the middle of the tube, until finally the whole tube is heated. The heating must be gradual, so that the combustion is not too rapid, or some of the products may pass through the absorption-bulbs unabsorbed. When the combustion is completed the liquid in the bulb of the Geissler's bulbs nearest the calcium chloride tube will ascend. An aspirator is attached to the Geissler's bulbs, and a rubber tube leading to a drying apparatus is attached to the bayonet-like end of the combustion-tube, the end of the glass tube broken off while in the rubber tube, and the aspirator started. Oxygen or air, free from CO_2 or H_2O , is slowly drawn through the combustion-tube to burn any of the organic compound which may have escaped decomposition, and also to convey any CO_2 or vapor of H_2O remaining in the combustion-tube into the Geissler's bulbs and calcium chloride tube. The drying apparatus through which the oxygen or air is caused to pass before entering the combustion-tube is composed of a

series of three cylinders, the first containing a solution of KOH to absorb CO_2 ; the second and third containing respectively sulphuric acid and pieces of calcium chloride to absorb H_2O . After drawing oxygen or air through the tube a few minutes the flames are extinguished, the Geissler's bulbs and the calcium chloride tube are detached (the openings stoppered) and allowed to cool. When cool they are unstoppered and weighed. The increase in weight of the Geissler's bulbs containing the KOH will indicate the quantity by weight of CO_2 which resulted from the combustion of the carbon in the organic substance employed.

The increase in weight of the tube containing calcium chloride will indicate the quantity by weight of H_2O which resulted from the combustion of the hydrogen in the organic substance employed.

The quantity of carbon is calculated from the weight of CO_2 obtained, as follows :

$$\overset{44}{\text{CO}_2} : \overset{12}{\text{C}} :: \text{wt. of CO}_2 \text{ obtained} : \text{X}$$

The quantity of hydrogen is calculated from the weight of H_2O obtained, as follows :

$$\overset{18}{\text{H}_2\text{O}} : \overset{2}{\text{H}_2} :: \text{wt. of H}_2\text{O obtained} : \text{X}$$

If the compound for analysis be a liquid, it is placed in a small weighed glass bulb having a drawn-out tube. This is accomplished by rarefying the air in the bulb by heating and holding the drawn-out end in the liquid. On cooling, the liquid will ascend and occupy the space of the expelled air. The tube is then sealed over a Bunsen flame and the bulb weighed. The increase of weight is the weight of the compound contained in the bulb. The bulb containing the liquid is dropped into the combustion-tube containing the cupric oxide, and the method proceeds as before.

If the compound to be analyzed contain nitrogen in addition to the carbon and hydrogen or oxygen, oxides of nitrogen may be formed during the combustion, and these oxides being absorbed with the CO_2 by the KOH solution in the Geissler's bulbs, would lead to inaccurate results by apparently increasing the quantity of CO_2 . In this case, metallic copper (in the form of turnings or gauze) is heated in a current of hydrogen and then placed in the combustion-tube, at the end at which

the calcium chloride tube is attached, in order to decompose the oxides of nitrogen into free oxygen and nitrogen.

If sulphur be present in the compound, SO_3 (sulphuric anhydride) may be formed in the combustion and be absorbed with the CO_2 by the KOH in the Geissler's bulbs. In this case, PbO_2 (lead dioxide) should be placed in the combustion-tube containing the cupric oxide, at the end at which the calcium chloride tube is attached. The SO_3 will combine with, and be held by, the lead as PbSO_4 . Lead dioxide need not be placed in the tube if lead chromate is used in the combustion instead of cupric oxide.

Compounds containing chlorine, iodine, or bromine when burned with cupric oxide form cupric chloride, iodide, or bromide, which volatilize at a high temperature and condense in the calcium chloride tube, thus causing a fictitious increase in the weight of the H_2O . Compounds containing these elements must be burned with lead chromate (PbCrO_4); non-volatile plumbic chloride, iodide, or bromide will be formed and retained in the combustion-tube.

Compounds difficult of combustion should be burned with lead chromate or with pure oxygen. The latter is employed especially for coals and coke. The substance to be burned is placed in a porcelain boat, and, instead of glass, an iron combustion-tube is often employed.

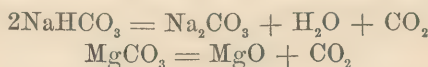
METHODS: ESTIMATION OF NITROGEN.

1. *Dumas's method*: Depends upon the decomposition of the organic substance with the evolution of all of the nitrogen, which is collected and measured in a eudiometer.

The nitrogenous compound is burned in a combustion-tube with cupric oxide and copper wire gauze as in the estimation of carbon and hydrogen, except that a layer of about three inches of acid sodium carbonate (NaHCO_3) or of magnesite (magnesium carbonate, MgCO_3) is placed at the closed end of the tube. When filled the tube contains the following substances in the given order:

1. NaHCO_3 or MgCO_3 (to the depth of about three inches).
2. Cupric oxide (nearly to the middle of the tube).
3. Mixture of organic substance and cupric oxide.
4. Cupric oxide.
5. Copper gauze to decompose oxides of nitrogen.

A delivery-tube is attached to the open end of the combustion-tube (the exit of the delivery-tube being brought below the surface of mercury contained in a trough), and a glass tube, containing mercury and a solution of sodium hydroxide, is inverted over the exit of the delivery-tube. The acid sodium carbonate, or the magnesium carbonate is heated first. Decomposition takes place and CO_2 is evolved.



The heating of the carbonate is continued until all the air is driven out of the combustion-tube by CO_2 . This is accomplished when the bubbles of evolved gas are completely absorbed by the KOH solution.

When all the air is driven out, the heating of the carbonate is discontinued, and the KOH tube is removed. A eudiometer, containing mercury and a layer (about three or four inches in thickness) of solution of KOH, is now inverted over the exit of the delivery-tube. Heat is applied to the end of the tube (No. 5) containing the copper gauze, and also to the part containing cupric oxide (No. 2) next to the carbonate. The heat is gradually extended to the middle of the tube, until the entire tube, except (No. 1) carbonate part, is heated. The heating is discontinued when gas-bubbles cease to come over into the eudiometer.

At this point the acid sodium carbonate is again heated, more CO_2 is evolved which drives out the remaining nitrogen. The heating is continued until the gas-bubbles entering the eudiometer are completely absorbed by the KOH.

The CO_2 and H_2O produced in the combustion are absorbed by the solution of KOH. The nitrogen is not absorbed, and collects in the upper part of the eudiometer.

The eudiometer containing the nitrogen is transferred to a vessel of water, the atmospheric pressure is equalized, and the volume of nitrogen read off and corrected for temperature and pressure.

$$14 \text{ grm. nitrogen} = 11160 \text{ c.c.}$$

$$11160 : 14 :: 1 \text{ c.c.} : 0.001256$$

1 c.c. of nitrogen at 0°C. and 760 mm. weighs 0.001256 grm.

2. *Will's and Varrentrapp's method*: Depends upon the formation of NH_3 (ammoniacal gas) when an organic substance containing nitrogen is heated with soda-lime.

This method is not applicable for the estimation of nitrogen in compounds in which the nitrogen is present as a nitro group.

A combustion-tube is nearly half-filled with dry soda-lime. The weighed organic substance is added and thoroughly mixed by means of a wire stirrer with the soda-lime. More soda-lime is added until the tube is within about an inch of being filled, and a plug of loose asbestos is placed in the end.

The tube now contains the following substances in the order given :

1. Soda-lime.
2. Mixture of organic substance and soda-lime.
3. Soda-lime.
4. Plug of loose asbestos.

a. Gravimetrically.

The combustion-tube is connected with Will's bulbs, containing dilute hydrochloric acid, and is heated in a combustion-furnace. The heating should be commenced simultaneously at each end of the tube, and gradually extended to the middle.

The NH_3 is absorbed by the HCl in the Will's bulbs, forming NH_4Cl .

The contents of the Will's bulbs are emptied into a dish; excess of platinum chloride, which precipitates the ammonia, is added, and the whole evaporated to dryness on a water-bath. The residue is collected on a weighed filter by means of a mixture of alcohol and ether, and thoroughly washed with a mixture of the same liquid.

When the precipitate, $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$, is dry it is weighed. Every 100 parts of $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$ contains 6.313 parts of nitrogen.

$$\begin{array}{rcl} (\text{NH}_4\text{Cl})_2\text{PtCl}_4 & \text{N}_2 & \\ 443.5 & : 28 & :: 100 : 6.313 \end{array}$$

or the quantity of nitrogen may be calculated as follows :

$$\begin{array}{rcl} (\text{NH}_4\text{Cl})_2\text{PtCl}_4 & \text{N}_2 & \\ 443.5 & : 28 & : \text{weight of precipitate} : X \end{array}$$

Instead of weighing the precipitate as $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$, it may be incinerated and weighed as metallic platinum; then

Every 100 parts of platinum are equivalent to 14.395 parts of nitrogen.

$$\begin{array}{rcl} \text{Pt.} & \text{N}_2 & \\ 194.5 & : 28 & :: 100 : 14.395 \end{array}$$

or the quantity of nitrogen may be calculated as follows :

Pt. N₂.
194.5 : 28 :: weight of metallic platinum : X

b. Volumetrically.

A measured volume of a normal solution of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$) may be used in the Will's bulbs, instead of dilute HCl, to absorb the NH_3 , and the quantity of nitrogen calculated from the number of cubic centimetres of oxalic acid solution, neutralized by the NH_3 , as determined by titrating with a normal solution of NaOH.

$\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$, a dibasic acid.

$$\frac{126}{2} = 63$$



$$\begin{array}{ccc} \text{Oxalic acid.} & & \text{NH}_3. \\ 126 \text{ grm.} & = & 34 \text{ grm.} \\ 63 \text{ " } & = & 17 \text{ " } \end{array}$$

A normal solution of oxalic acid is prepared by dissolving 63 grm. of pure oxalic acid in 1000 c.c. water; then

$$\begin{array}{ccccccc} & \text{Oxalic acid.} & & \text{NH}_3. & & \text{N.} & \\ 1000 \text{ c.c.} & = & 63.0 \text{ grm.} & = & 17.0 \text{ grm.} & = & 14.0 \text{ grm.} \\ 1 \text{ c.c.} & = & 0.063 \text{ " } & = & 0.017 \text{ " } & = & 0.014 \text{ " } \end{array}$$

10 c.c. of the oxalic acid solution are placed in the Will's bulbs. The combustion of the organic compound is performed, and the NH_3 evolved is absorbed by the oxalic acid solution.

When the combustion is completed the oxalic acid solution in the Will's bulbs is emptied into a beaker, a few drops of litmus added, and the oxalic acid titrated with a normal solution of NaOH.

1000 c.c. of normal sol. of NaOH contains 40.0 grm. NaOH.

$$1 \text{ c.c. " " " " " " } = 0.040 \text{ " "}$$

$$0.040 \text{ NaOH} = 0.063 \text{ oxalic acid.}$$

Consequently 1 c.c. normal solution of NaOH is equal to (will neutralize) 1 c.c. normal oxalic acid solution, and 10 c.c. normal NaOH solution are equal to 10 c.c. normal oxalic acid solution.

On titrating the 10 c.c. oxalic acid solution from the Will's bulbs, it will now be found that less than 10 c.c. of normal NaOH solution will be required, showing that some of the oxalic acid solution has been neutralized by the NH_3 .

Suppose only 6 c.c. of normal NaOH solution were required to neutralize the 10 c.c. oxalic acid solution from the Will's

bulbs, then the difference between 6 and $10 = 4$ indicates the number of cubic centimetres of oxalic acid solution neutralized by the NH_3 arising from the combustion of the organic compound.

1 c.c. of oxalic acid solution is neutralized by 0.017 NH_3 , equivalent to 0.014 N, and as 4 c.c. were neutralized then $4 \times 0.014 = 0.056$ grm. nitrogen present in the weight of organic compound analyzed,

3. *Kjeldahl's method*: Depends upon the conversion of the nitrogen in a compound into ammonia, by boiling it with sulphuric acid. The ammonia combines with the sulphuric acid to form ammonium sulphate. The ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$, is decomposed into NH_3 and Na_2SO_4 by boiling it with sodium hydroxide. The evolved ammoniacal gas (NH_3) is collected in dilute hydrochloric acid and precipitated with platinum chloride as $(\text{NH}_4\text{Cl})_2\text{PtCl}_4$.

The precipitate is collected on a filter, washed with a mixture of alcohol and ether, and treated exactly as in Will's and Varrentrapp's method.

The NH_3 may also be collected in a measured volume of normal oxalic acid solution and titrated with a normal solution of sodium hydroxide, as in Will's and Varrentrapp's method.

ESTIMATION OF SULPHUR.

Sulphur in an organic compound is estimated quantitatively by fusing the compound with about 12 parts of potassium hydroxide (KOH) and 6 parts of potassium nitrate (KNO_3), or by boiling the compound with nitric acid, as in the qualitative detection of sulphur. The sulphur is oxidized to sulphuric acid, the latter is precipitated with barium chloride (BaCl_2) as barium sulphate (BaSO_4), and the quantity of sulphur is calculated from the amount of BaSO_4 obtained.

$$233 \text{ parts of } \text{BaSO}_4 = 32 \text{ parts of S.}$$

ESTIMATION OF PHOSPHORUS.

Phosphorus is estimated quantitatively by fusing the compound with the usual mixture of KOH and KNO_3 , or by boiling it with HNO_3 , as in the estimation of sulphur. The phosphorus is oxidized to phosphoric acid, which is precipitated by the magnesia mixture ($\text{NH}_4\text{Cl} + \text{NH}_4\text{HO} + \text{MgSO}_4$), and weighed as magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$.

$$222 \text{ parts of } \text{Mg}_2\text{P}_2\text{O}_7 = 62 \text{ parts of P.}$$

ESTIMATION OF CHLORINE, BROMINE, AND IODINE.

Chlorine, bromine, and iodine are estimated quantitatively by heating the compound in a combustion-tube with caustic lime, as in the qualitative detection of these elements, precipitating with argentic nitrate (AgNO_3), and weighing as argentic chloride (AgCl), argentic bromide (AgBr), and argentic iodide (AgI).

CALCULATION OF RESULTS AND DEDUCTION OF FORMULAS.

Determine the percentages of all the elements in the compound. Divide the percentage of each element by its atomic weight. Then divide the quotients obtained by the smallest quotient, and, if necessary, multiply these final quotients by the least number that will make all of them whole or nearly whole numbers. The formula thus obtained is the empirical formula, and at the same time may be the molecular formula. The molecular formula is determined by observing the vapor density of the compound, etc.

Example: A combustion of 0.340 grm. of *oil of turpentine*, a compound containing only carbon and hydrogen, furnished

CO_2 , 1.100 grm.

H_2O , 0.360 "

then, $\begin{array}{cccc} \text{CO}_2. & \text{C.} & \text{Wt. of CO}_2. & \text{C.} \\ a. & 44 : 12 :: 1.100 : 0.300 \text{ grm.} \end{array}$

$\begin{array}{cccc} \text{H}_2\text{O.} & \text{H}_2. & \text{Wt. of H}_2\text{O.} & \text{H.} \\ & 18 : 2 :: 0.360 : 0.040 \text{ grm.} \end{array}$

Hence 0.340 grm. of the oil contained

0.300 carbon.

0.040 hydrogen.

$\begin{array}{cc} \text{oil.} & \text{C.} \\ b. & 0.340 : 0.300 :: 100 : 88.235 \text{ per cent. carbon.} \end{array}$

$\begin{array}{cc} \text{oil.} & \text{H.} \\ & 0.340 : 0.040 :: 100 : 11.765 \text{ per cent. hydrogen.} \end{array}$

The percentage composition is,—

Carbon, 88.235

Hydrogen, 11.765

100.000

$c. 88.235 \div 12 = 7.353 \div 7.353 = 1 \times 5 = 5 \text{ atoms C.}$

$11.765 \div 1 = 11.765 \div 7.353 = 1.599 \times 5 = 7.995 \text{ atoms H,}$

or, approximately, 8 atoms of H.

Hence the empirical formula of oil of turpentine is C_5H_8 .
(The molecular formula is twice C_5H_8 , or $\text{C}_{10}\text{H}_{16}$.)

Or, if 0.340 grm. oil of turpentine furnished

CO₂, 1.100 grm.

H₂O, 0.360 "

then,
$$\begin{array}{ccc} \text{Oil.} & \text{CO}_2 & \text{CO}_2 \\ a. & 0.340 : 1.100 :: 100 : 323.53 \text{ grm.} \end{array}$$

$$\begin{array}{ccc} \text{Oil.} & \text{H}_2\text{O.} & \text{H}_2\text{O.} \\ & 0.340 : 0.360 :: 100 : 105.88 \text{ grm.} \end{array}$$

If 100 grm. of the oil yields 323.53 grm. CO₂ and 105.88 grm. H₂O, then to obtain the percentage proportion of carbon and hydrogen,—

$$\begin{array}{ccc} \text{CO}_2 & \text{C.} & \\ b. & 44 : 12 :: 323.53 : 88.235 \text{ per cent. carbon.} \end{array}$$

$$\begin{array}{ccc} \text{H}_2\text{O.} & \text{H}_2. & \\ & 18 : 2 :: 105.88 : 11.765 \text{ per cent. hydrogen.} \end{array}$$

And from these percentages of carbon and hydrogen we find,—

c. $88.235 \div 12 = 7.353 \div 7.353 = 1 \quad \times 5 = 5 \text{ atoms C.}$

$11.761 \div 1 = 11.765 \div 7.353 = 1.599 \times 5 = 7.995 \text{ atoms H,}$
or, approximately, 8 atoms of H.

Hence the empirical formula for the compound is C₅H₈.

Oxalic acid is composed of,—

Carbon, 26.66 per cent.

Hydrogen, 2.22 "

Oxygen, $\frac{71.12}{100.00}$ "

Then,

C $26.66 \div 12 = 2.22 \div 2.22 = 1 \text{ atom carbon.}$

H $2.22 \div 1 = 2.22 \div 2.22 = 1 \quad \text{" hydrogen.}$

O $71.12 \div 16 = 4.44 \div 2.22 = 2 \quad \text{" oxygen.}$

Hence its empirical formula is HCO₂. (The molecular formula is twice HCO₂, or H₂C₂O₄.)

Composition of cane sugar according to Liebig,—

Carbon, 42.30 = 1.001

Hydrogen, 6.45 = 2.009

Oxygen, $\frac{51.25}{100.00} = 1.000$

Formula for cane sugar according to different chemists,—

Berzelius, C₁₂H₂₂O₁₁.

Doebereiner, C₆H₁₂O₆.

Dumas, C₅H₁₀O₅.

Prout, C₈H₁₆O₈.

THE URINE.

The *urine* is the secretion of the kidneys, in which effete nitrogenized products are thrown out from the system.

The normal color is yellow. The intensity of color is proportionate to the specific gravity, except diabetic urine, in which the specific gravity may be high and the color pale yellow.

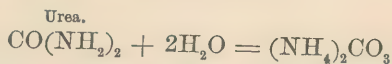
The *reaction* of normal urine just voided is usually *acid*. The *acid reaction* is not due to the presence of free acid but to acid salts, principally to acid sodium phosphate (NaH_2PO_4), arising from the sodium phosphate (Na_2HPO_4) of the blood coming in contact with the uric acid of the urine.

Neutral sodium phosphate. Uric acid. Acid sodium phosphate. Neutral sodium urate.
 $2\text{Na}_2\text{HPO}_4 + \text{H}_2\text{C}_5\text{H}_2\text{N}_4\text{O}_3 = 2\text{NaH}_2\text{PO}_4 + \text{Na}_2\text{C}_5\text{H}_2\text{N}_4\text{O}_3$

It may be voided having an alkaline reaction, especially after a very hearty meal, and also after the ingestion of alkalies and substances, as the acetates, tartrates, and citrates (lemon-juice) of the alkalies, which in the organism are converted into and voided as alkaline carbonates.

On the ingestion of acids the urine may be voided having a strong acid reaction.

Normal urine, on standing some time, may become alkaline in reaction, due to the presence of ammonium carbonate, resulting from the action of certain micro-organisms (*micrococcus ureæ*) on the urea.



Normal urine may have an amphoteric reaction,—*i.e.*, changing blue litmus-paper to red, and red litmus to blue,—due to the simultaneous presence in the urine of acid and neutral phosphates.

The acidity of the average quantity of urine voided in a day will require from 1.0 to 1.5 grm. NaOH to neutralize it.

The average quantity of sodium acid phosphate (NaH_2PO_4) daily eliminated in the urine is equivalent to about 2.3 grm. phosphoric anhydride (P_2O_5), and to convert 2.3 grm. P_2O_5 as NaH_2PO_4 into Na_2HPO_4 will require 1.3 grm. NaOH.

The *acidity of the urine* is determined by means of a decinormal solution of sodium hydroxide (NaOH).

A normal solution of NaOH contains 40.0 grm. of NaOH per 1000 c.c. A deci-normal solution contains $\frac{1}{10}$ of 40.0, or 4.0 grm. of NaOH per 1000 c.c.

$$\begin{array}{rcl} & \text{NaOH.} & \\ 1000 \text{ c.c.} & = & 4.0 \text{ grm.} \\ 1 \text{ c.c.} & = & 0.004 \text{ "} \end{array}$$

Method: To 100 c.c. of urine, add two or three drops of rosolic acid, or of litmus solution, run in deci-normal solution of NaOH from a burette until a change takes place in the color of the indicator (rosolic acid, or litmus), read off the number of c.c. NaOH solution required, and multiply this number by the value of 1 c.c. of the deci-normal solution expressed in NaOH units,—namely, 0.004.

Example:

100 c.c. urine requires 30 c.c. NaOH solution.

$30 \times 0.004 = 0.120$ NaOH required for 100 c.c. urine.

$12 \times 0.120 = 1.440$ grm. NaOH required for 1200 c.c. (daily quantity) of the urine.

Specific Gravity of Urine.—The specific gravity of normal urine varies from 1015 to 1025. The average is about 1017,—water taken as 1000.

The specific gravity may be as low as 1003 or even lower, and 1030 or higher.

The specific gravity may be determined by—

a. Urinometer.

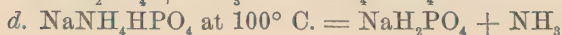
b. Specific gravity bottle (picnometer).

The specific gravity is affected by temperature. It should be taken with the liquid at a temperature of 15° C. or 60° F.

The specific gravity is lowered one unit (the specific gravity of water expressed as 1000) for every increase of 3° C. temperature.

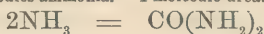
Determination of Quantity of Solid Matter in Urine.—1. A ready method is to evaporate 10 c.c. urine in a weighed dish to dryness on a water-bath. Dry the residue in a drying-oven at 100° C., place in a dessicator, weigh, and repeat the drying operation and weighing until a constant weight is obtained. The weight, minus the weight of the dish, is the amount of solid matter in 10 c.c. of the urine.

This method is not very accurate, because during the evaporation some of the urea is decomposed with the evolution of ammoniacal gas (NH_3), as—



2. An *accurate method* is to evaporate to dryness 2 c.c. urine in a weighed porcelain boat in Neubauer's special drying apparatus. Collect the evolved NH_3 in normal sulphuric acid solution, and determine the quantity of the latter neutralized by the NH_3 by means of a normal NaOH solution, and from the quantity neutralized deduce the equivalent of urea.

2 molecules ammonia. 1 molecule urea.



Or,

34 parts of ammonia = 60 parts of urea.

3. The solid matter may be approximately determined by multiplying the last two figures of the specific gravity by Haeser and Neubauer's factor, 2.33. Thus if specific gravity is 1017,

$$17 \times 2.33 = 39.61 \text{ grm. solid matter in 1000 c.c. of the urine.}$$

Or more closely (if the specific gravity be expressed with five figures), by multiplying the last three figures by the factor 0.233. Thus if the specific gravity is 1020.3,

$$203 \times 0.233 = 47.299 \text{ grm. solid matter in 1000 c.c. of the urine.}$$

AVERAGE COMPOSITION OF HUMAN URINE.

				Voided per day.	
				Grains.	Grammes.
Water	.	.	950.00		
Urea	.	.	28.00	520.80	35.00
Uric acid	.	.	0.60	37.60	Organic matter.
Hippuric acid	.	.	0.35		
Creatinine	.	.	0.65		
Extractives	.	.	8.00		
Sodium chloride	.	.	8.00	148.80	10.00
Phosphoric acid	.	.	2.00	37.20	2.50
Sulphuric acid	.	.	1.25	12.40	Inorganic matter.
Lime (CaO)	.	.	0.25		
Magnesia (MgO)	.	.	0.30		
Potash (K_2O) and soda (Na_2O)	.	.	0.60		
			1000.00	930.20	62.49
Water	.	.	950.00		
Organic matter	.	.	37.60	699.36	47.00
Inorganic matter	.	.	12.40	230.64	15.49

Average quantity of urine voided per day, about 40 fluid-ounces, or 1200 c.c.

ANALYSIS OF THE URINE.

The analysis of urine may have for its object—

1. The *qualitative* detection of the normal and abnormal constituents.

2. The *quantitative* determination of the normal and abnormal constituents.

The percentages in urine are expressed as percentage by volume,—i.e., 100 c.c. by volume contain a given weight of a solid.

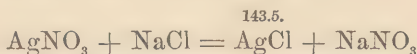
ESTIMATION OF SODIUM CHLORIDE (NaCl) IN URINE.

The chlorine in urine is in combination as a chloride, chiefly as sodium chloride (NaCl).

It may be detected qualitatively by strongly acidulating the urine with nitric acid and adding a solution of argentic nitrate (AgNO_3). If NaCl be present in rather large quantity, a curdy precipitate of argentic chloride (AgCl) will be formed; if the quantity present be small, only a milkiness will be produced. If the urine contain albumen, it must be removed before making this test.

QUANTITATIVE ESTIMATION OF SODIUM CHLORIDE.

1. *Gravimetric method.* Principle: when argentic nitrate (AgNO_3) is added to sodium chloride (NaCl) all of the chlorine is precipitated as argentic chloride (AgCl).



The quantity of sodium chloride, or of chlorine, is calculated from the quantity of AgCl obtained.

Every 143.5 parts of $\text{AgCl} = 58.5 \text{ NaCl}$ or 35.5 Cl.

Hence $\overset{\text{AgCl.}}{143.5} : \overset{\text{NaCl.}}{58.5} :: \text{weight of precipitate of } \overset{\text{NaCl.}}{\text{AgCl}} : X$

Or,

$\overset{\text{AgCl.}}{143.5} : \overset{\text{Cl.}}{35.5} :: \text{weight of precipitate of } \overset{\text{Cl.}}{\text{AgCl}} : X.$

Method: Evaporate 10 c.c. urine with about 2 grm. potassium nitrate (KNO_3) to dryness in a dish on a water-bath (*absolute* dryness cannot be obtained) or over a flame, being careful to avoid loss from spurting. (Do not stir with a glass rod or by any other means.) Heat the residue over a flame, very gently at first, then with strong heat, until all the organic

matter is destroyed. Allow to cool, dissolve the residue with 5 c.c. water, adding eight or ten drops strong nitric acid. Warm the liquid in a dish to hasten solution. Pour this first portion, 5 c.c., into a beaker (keeping back any enamel that may have separated from the dish), and repeat the washing with portions of 5 c.c. water (without further addition of nitric acid), heating, if necessary, until the dish has been thoroughly washed. Pour each portion of 5 c.c. into the beaker until 30 c.c. have been employed and collected in the beaker. If the liquid is not acid in reaction, acidulate with nitric acid. Warm the solution, and add excess of AgNO_3 solution. Stir the liquid with a glass rod until the precipitate separates in curds. Collect it on a filter, wash until the filtrate shows no trace of the presence of silver (test with HCl). Dry the precipitate while still on the filter, detach as much as is possible, and place in a weighed crucible. Burn the filter, holding it over, and allowing the ash to fall into, the crucible. Moisten the ash with two or three drops of strong nitric acid to dissolve the metallic silver which may have resulted from the reduction of AgCl in burning the filter, and warm the crucible very gently. When cool, moisten the ash with two or three drops of hydrochloric acid to reprecipitate, as chloride, the silver dissolved by the nitric acid. Drive off excess of acid by gently heating over a very small flame. Weigh when cool. Deduct weight of crucible and ash, the remainder is AgCl .

Calculation:

AgCl. NaCl.

143.5 : 58.5 :: weight of precipitate of AgCl : X = quantity of *sodium chloride* in the volume (10 c.c.) of urine employed. Multiply by 10 = percentage of NaCl .

Or,

AgCl. Cl.

143.5 : 35.5 :: weight of precipitate of AgCl : X = quantity of *chlorine* in the 10 c.c. urine employed. Multiply by 10 = percentage of chlorine.

Example: If 0.200 grm. AgCl obtained, then

AgCl. NaCl. wt. of prec. NaCl. NaCl.

143.5 : 58.5 :: 0.200 : $0.08153 \times 10 = 0.8153$ per cent. in a volume of 100 c.c. urine.

But in a weight of 100 grm. of urine,

Say specific gravity of urine 1020 : 1000 :: 0.815 : 0.799 per cent. in 100 grm. of the urine.

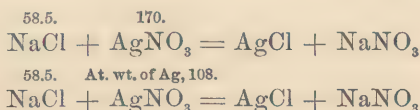


2. *Mohr's volumetric method for the estimation of sodium chloride:*
Depends upon the precipitation of the chlorine of the sodium chloride by means of a standard solution of argentic nitrate.

The standard solution of argentic nitrate is prepared of convenient strength,—i.e., so that 1 c.c. of the solution shall equal 0.010 of NaCl. 1 c.c. of the solution is also equal to 0.006068 chlorine,—i.e.,

$$\begin{array}{cccc} \text{NaCl.} & \text{Cl.} & \text{Cl.} & \text{Cl.} \\ 58.5 & : 35.5 & :: 0.010 & : 0.006068 \end{array}$$

Preparation of the standard solution of AgNO_3 :



170 grm. of AgNO_3 are equal to 58.5 grm. of NaCl.

170 grm. of AgNO_3 (equal to 58.5 grm. NaCl) contain 108 grm. of metallic silver, consequently 108 grm. of silver are also equal to 58.5 grm. of NaCl.

The quantity of AgNO_3 necessary to prepare 1000 c.c. of standard solution so that 1 c.c. of it shall equal 0.010 NaCl or 0.006068 Cl is determined by

$$\begin{array}{cccc} \text{NaCl.} & \text{AgNO}_3. & \text{grm. NaCl.} & \text{AgNO}_3. \\ 58.5 & : 170 & :: 10 & : 29.059 \text{ grm.} \end{array}$$

Or of metallic silver to be converted into nitrate, by treating with nitric acid, evaporating excess of acid, and dissolving the residue in water, and diluting to 1000 c.c.

$$\begin{array}{cccc} \text{NaCl.} & \text{Ag.} & \text{grm. NaCl.} & \text{Metallic silver.} \\ 58.5 & : 108 & :: 10 & : 18.461 \text{ grm.} \end{array}$$

Preparation of standard solution of argentic nitrate:

Dissolve 29.059 grammes pure AgNO_3 in distilled water and dilute with distilled water to a volume of 1000 c.c.

Or, dissolve 18.461 grammes pure metallic silver in nitric acid, evaporate excess of acid, and dissolve the residue (which is AgNO_3) in distilled water, and dilute with water to 1000 c.c. Then,

$$\begin{array}{ccc} & \text{AgNO}_3. & \text{NaCl.} \\ 1000 \text{ c.c.} & = 29.059 & \text{grm.} = 10.0 \\ 10 \text{ c.c.} & = 0.29059 & \text{"} = 0.100 \\ 1 \text{ c.c.} & = 0.029059 & \text{"} = 0.010 \\ & & \text{Chlorine.} \\ 1 \text{ c.c.} & = 0.029059 & \text{"} = 0.006068 \end{array}$$

Sometimes it is necessary to prove the accuracy of the solution by standardizing it with a standard solution of sodium chloride.

Dissolve 1.0 gram. NaCl in water and dilute to 100 c.c.

$$\begin{array}{rcl} & \text{NaCl.} & \\ 100 \text{ c.c.} & = & 1.0 \text{ gram.} \\ 10 \text{ c.c.} & = & 0.100 \text{ " } \\ 1 \text{ c.c.} & = & 0.010 \text{ " } \end{array}$$

a. To 10 c.c. of the NaCl solution add two drops of potassium chromate (K_2CrO_4) solution (the indicator), and run the AgNO_3 solution into it from a burette until the lemon-yellow color of the liquid is changed to a very slight orange-red. The red color is due to the formation of red argentic chromate (Ag_2CrO_4), and indicates that all of the NaCl has been decomposed and a slight excess of the AgNO_3 solution has acted on the potassium chromate present.

Suppose 10.4 c.c. AgNO_3 are required, then add $\frac{4}{100}$ of 29.059 gram. AgNO_3 to the AgNO_3 solution, after having deducted $\frac{1}{100}$ from the quantity (*i.e.*, from $\frac{4}{100}$ of 29.059 gram.) to allow for the 10.4 c.c. of the AgNO_3 used in the standardizing.

$$\frac{4}{100} \text{ of } 29.059 = 1.16236 \text{ minus } \frac{1}{100}, \text{ or } 0.01162 = 1.1507 \text{ gram.}$$

AgNO_3 to be added to the 989.6 c.c. silver solution remaining.

If the AgNO_3 solution is thus standardized and the residue from 10 c.c. urine is dissolved in 30 c.c. water, then, in actual analysis, because of increased dilution, deduct 0.2 c.c. (0.1 for every 10 c.c. above a fixed 10 c.c.) from the number of c.c. AgNO_3 solution required.

b. The AgNO_3 solution may be standardized so that in actual analysis no correction (deduction of 0.2 c.c.) will be necessary.

Dilute 10 c.c. standard solution of NaCl (containing 0.100 gram. NaCl) with 20 c.c. water, so that the volume (30 c.c.) shall equal the volume of the final solution in the actual work with the urine. Add two drops of K_2CrO_4 solution, and run the AgNO_3 solution from a burette into the NaCl solution until the lemon-yellow color of the liquid is changed to a slight orange-red.

Suppose 10.4 c.c. of AgNO_3 solution have been required for the 0.100 gram. NaCl in the solution. The silver solution should be arranged so that 10 c.c. shall be required for the 0.100 gram. NaCl in the 30 c.c. of liquid. Add $\frac{4}{100}$ of 29.059 gram. AgNO_3 , minus $\frac{1}{100}$, or 1.1507 gram. AgNO_3 , to the 989.6

c.c. silver solution remaining (as in method *a*). 10 c.c. of the AgNO_3 solution will now equal 0.100 gram. NaCl dissolved in 30 c.c. water, and 1 c.c. = 0.010 gram. NaCl . When the solution is standardized in this manner no further correction is necessary, provided the volume of liquid operated upon is 30 c.c.

c. Instead of calculating the quantity of AgNO_3 to be added to a standard solution that is too weak,—i.e., one requiring the addition of *more* than 10 c.c. of the AgNO_3 solution for 0.100 grm. NaCl ,—the solution may be corrected by adding more AgNO_3 , thereby making it too strong, and then adding the volume of water to dilute it to the proper strength.

d. The standard solution may be too strong, *i.e.*,—requiring the addition of *less* than 10 c.c. of the AgNO_3 for 0.100 grm. NaCl . It may be corrected by determining and adding the volume of water to dilute it to the proper strength.

Suppose 8 c.c. instead of 10 c.c. of the AgNO_3 solution have been required for the 0.100 grm. NaCl . To every 8 c.c. of standard solution remaining add a volume of water equal to the difference between 8 and 10 c.c., or 2 c.c.

1000 c.c. solution prepared.

8 c.c. used.

8)992 c.c. on hand.

$$124 \times 2 = 248 \text{ c.c. water to be added to}$$

the 992 c.c. standard solution.

10 c.c. will now equal 0.100 grm. of NaCl.

1 c.c. " " 0.010 " "

Method: Evaporate 10 c.c. urine with about 2 grm. KNO_3 to dryness in a small dish. (Do not stir with a glass rod or by any other means). Heat the residue over a flame, gently at first, then with strong heat, until the organic matter is decomposed. Allow to cool, dissolve the residue with 5 c.c. water, adding 8 or 10 drops of strong nitric acid. Warm the liquid in the dish to hasten solution. Pour this first portion of 5 c.c. into a beaker (paying no attention to any enamel which may have separated from the dish) and repeat the washings with separate portions of 5 c.c. water (without further addition of nitric acid), heating, if necessary, until the dish has been thoroughly washed. Pour each portion of 5 c.c. into the beaker until 30 c.c. of water have been employed and collected in the beaker. If the liquid

is not acid in reaction, acidulate very slightly with nitric acid. (Up to this point, except disregarding the enamel, the method is practically the same as in the gravimetric method).

Neutralize by adding excess of precipitated calcium carbonate (CaCO_3), and add two drops of potassium chromate solution (indicator).

Run the AgNO_3 solution from a burette into the 30 c.c. liquid containing the NaCl until the lemon-yellow color is changed to a slight orange-red.

Read off the number of cubic centimetres AgNO_3 solution required, and multiply this number by the value of 1 c.c. of the AgNO_3 solution expressed in terms of NaCl ,—namely, 0.010,—then multiply by 10 to obtain the percentage.

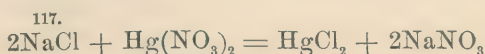
No correction is necessary, because the AgNO_3 solution employed has been standardized with a volume of 30 c.c. NaCl solution.

Suppose 8.3 c.c. AgNO_3 solution have been required. Then

$$8.3 \times 0.010 = 0.083 \text{ grm. NaCl in the 10 c.c. urine employed.}$$

$$0.083 \times 10 = 0.83 \text{ per cent. NaCl.}$$

3. *Liebig's method for the estimation of sodium chloride:* Depends upon the formation of a soluble salt of mercury (mercuric chloride, HgCl_2) on the addition of mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$) to a solution of sodium chloride.



The mercuric nitrate solution is prepared of such strength that 1 c.c. of it shall equal 0.010 grm. NaCl .

117 grm. NaCl require 200 grm. of mercury (once the atomic weight of Hg expressed in grammes).

Hence

$$\begin{array}{cccc} 2\text{NaCl.} & \text{Hg.} & \text{NaCl.} & \text{Hg.} \\ 117 : 200 :: 10 : 17.094 \text{ grm.} \end{array}$$

Or, 117 grm. NaCl require 216 grm. mercuric oxide (HgO) (once the molecular weight of HgO expressed in grammes).

$$\begin{array}{cccc} 2\text{NaCl.} & \text{HgO.} & \text{NaCl.} & \text{HgO.} \\ 117 : 216 :: 10 : 18.461 \text{ grm.} \end{array}$$

17.094 grm. of metallic mercury, or 18.461 grm. of mercuric oxide, are equal to 10 grm. NaCl .

PREPARATION OF STANDARD SOLUTION OF MERCURIC NITRATE.

Dissolve 17.044 *grm.* of mercury or 18.461 *grm.* of mercuric oxide with nitric acid and a little water, evaporate the excess of acid, and dissolve the residue with distilled water, and slowly dilute to 1000 c.c. If on dilution with water a canary-yellow precipitate of basic mercuric nitrate should separate, allow it to subside, pour off and preserve the supernatant liquid, dissolve the precipitate with a few drops strong nitric acid, and return the previously poured off supernatant liquid to the original vessel.

Hg(NO ₃) ₂ sol.	NaCl.	
1000 c.c. =	10.0	grm.
10 c.c. =	0.100	"
1 c.c. =	0.010	"
	Chlorine.	
1 c.c. =	0.006068	"

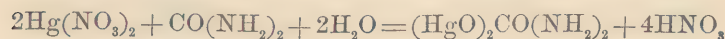
The mercuric nitrate solution may be standardized with a solution of NaCl containing 1.0 *grm.* NaCl in 100 c.c. water, using a pinch of urea as indicator.

Method: the phosphates, sulphates, and carbonates in the urine interfere with the application of the method. They are removed by the *baryta mixture*, composed of

2 volumes of a cold saturated solution of barium hydroxide (Ba(OH)₂).

1 volume of a cold saturated solution of barium nitrate (Ba(NO₃)₂).

The first action of the mercuric solution will be on the NaCl in the urine to form soluble HgCl₂; as soon as all the NaCl present has been decomposed, any excess of mercuric nitrate solution added will act upon the urea to form a white insoluble compound of mercuric oxide and urea, (HgO)₂CO(NH₂)₂,



and thus the urea acts as the indicator.

Method: mix 40 c.c. urine with 20 c.c. baryta mixture, filter through a *dry* filter, neutralize the filtrate with a drop or two of nitric acid. Transfer 15 c.c. of the filtrate (representing 10 c.c. urine and 5 c.c. baryta mixture) to a beaker and slowly run the mercuric nitrate solution into it, from a burette, until a permanent milky turbidity is produced. (Action on the urea.)

Multiply the number of cubic centimetres of mercuric solution required by 0.010 = quantity of NaCl in 10 c.c. urine, and this, multiplied by 10, gives the percentage.

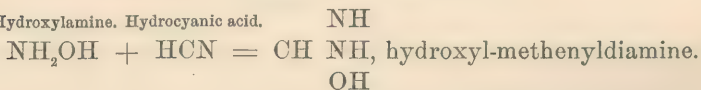
Liebig's method for the estimation of NaCl is now little used.

UREA. $\text{CO}(\text{NH}_2)_2$. *Molec. wt.*, 60.

CON_2H_4 , urea (but not NH_4CNO , ammonium cyanate). Generally considered to be $\text{CO}(\text{NH}_2)_2$, carbamide. Gamgee considers that it is not carbamide, because, when the latter is heated with potassium permanganate ($\text{K}_2\text{Mn}_2\text{O}_8$) and potassium hydroxide, all of its nitrogen is evolved as free nitrogen, whereas salts of ammonium (NH_4) and amides yield their nitrogen as N_2O_5 .

It is not isuretine, CON_2H_4 , because this is

Hydroxylamine. Hydrocyanic acid.



Urea was first recognized in the urine, and obtained in an impure state, by Rouelle, in 1773. Obtained in a purer condition, by Fourcroy and Vauquelin, in 1799. Prepared artificially, by Woehler, in 1828, it being the first organic compound produced artificially.

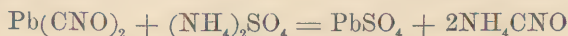
Urea is found in the urine of all mammals. It is smaller in quantity in the urine of birds and reptiles. Thirty per cent. of the solid matter of the vitreous humor of the eye is urea. It is contained in almost all the animal fluids,—blood, lymph, chyle, etc.,—and in the liver and spleen. It is the principal solid constituent of the urine. Ninety per cent. of the nitrogen eliminated by the urine is in the form of urea.

Urea may be prepared artificially by fusing and oxidizing potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) with manganese dioxide (MnO_2) or with minium ($\text{Pb}_3\text{O}_4 = 2\text{PbO} + \text{PbO}_2$), with the production of potassium cyanate (KCNO), which, when warmed with a solution of ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), forms ammonium cyanate (NH_4CNO), and by continued warming changes into urea ($\text{CO}(\text{NH}_2)_2$). The solution is evaporated to dryness on a water-bath, and the residue extracted with strong alcohol. The alcohol will dissolve only the urea, which may be obtained in crystalline form by allowing the alcohol to evaporate at ordinary temperature.



1. $K_4Fe(CN)_6 + O_9 = 4KCNO + 2CO_2 + FeO + N_2$
2. $2KCNO + (NH_4)_2SO_4 = 2NH_4CNO + K_2SO_4$
3. $NH_4CNO = CO(NH_2)_2$

It may also be prepared by warming plumbic cyanate ($Pb(CNO)_2$) with a solution of ammonium sulphate,



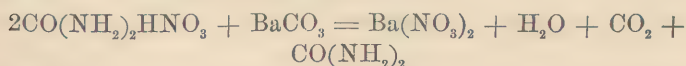
on further warming, the NH_4CNO is converted into urea.

UREA MAY BE OBTAINED FROM THE URINE BY THE FOLLOWING METHODS:

1. As *urea*: Add baryta mixture to the urine, filter, evaporate filtrate to dryness, treat residue with strong alcohol; filter and evaporate to dryness again, dissolve residue in water, and decolorize the solution by passing it through animal charcoal. Evaporate to dryness, and treat residue with strong alcohol. Filter and allow the alcohol to evaporate, and crystals of urea will appear.

2. As *urea nitrate*: Soluble in eight parts water.

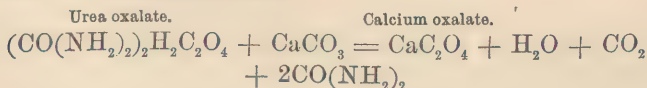
Evaporate about 250 c.c. (or more) urine to about one-sixth its original volume on a water-bath. When cold add nitric acid of about 1.25 specific gravity, and keep the mixture cold. Crystals of urea nitrate $CO(NH_2)_2HNO_3$ will separate. Collect the mass of crystals on a moistened piece of muslin, squeeze out the excess of liquid, and dissolve the mass in water. Add barium carbonate ($BaCO_3$) to the solution to separate the HNO_3 from the $CO(NH_2)_2HNO_3$.



Decolorize the solution by passing it through animal charcoal, evaporate the solution to dryness, treat the residue with strong alcohol, filter, and allow filtrate to evaporate to dryness at ordinary temperature. Crystals of urea will separate.

3. As *urea oxalate*: Soluble in twenty-five parts water.

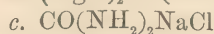
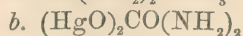
The method is similar to that with nitric acid, except that oxalic acid ($H_2C_2O_4$) (strong solution or in powder) is used instead of nitric acid, and calcium carbonate ($CaCO_3$) is used instead of barium carbonate.



Properties of Urea.—Urea is a white, odorless compound,

crystallizing in four-sided prisms. Has a cooling, bitter-like taste, somewhat resembling potassium nitrate. Very soluble in water, 1 to 1, soluble in alcohol, 1 to 5, insoluble in ether. Melts at a temperature of 130° C.

Urea in solution has no action on blue or red litmus-paper, is neutral, yet it will combine with acids, bases, and salts.



It unites with acids without displacing the hydrogen in the acid.

a. Urea in solution is decomposed by sodium hypochlorite with the evolution of CO_2 and N_2 .



b. Urea in solution is decomposed by nitrous acid (HNO_2) with the evolution of CO_2 and N_2 .

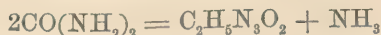


c. Urea heated with water in a glass tube sealed at both ends is converted into ammonium carbonate.



A like conversion occurs when urea is exposed for a time to the air, due to the action of micrococcus ureæ.

a. Urea in crystals heated to a temperature of 150°–170° C. fuses, ammonia (NH_3) is evolved, and a compound called biuret ($\text{C}_2\text{H}_5\text{N}_3\text{O}_2$) is produced.



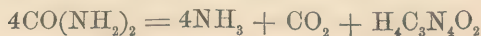
Biuret in solution produces a violet-red color on the addition of a solution of potassium or sodium hydroxide and a few drops of very dilute cupric sulphate solution. (Biuret reaction.)

Peptones and albumoses respond to the same test.

b. Urea heated to a higher temperature (over 170° C.) evolves ammonia, NH_3 , and cyanuric acid ($\text{H}_3\text{C}_3\text{N}_3\text{O}_3$) is produced.



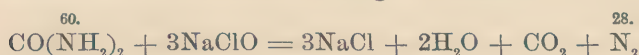
c. Urea heated to a still higher temperature evolves ammonia, and melanuric acid, $\text{H}_4\text{C}_3\text{N}_4\text{O}_2$ is produced.



QUANTITATIVE ESTIMATION OF UREA IN URINE.

1. *Davy's method*, introduced in 1854, depends upon the decomposition of the urea in the urine by means of sodium hypochlorite with the evolution of carbon dioxide and nitrogen. The CO_2 is absorbed by the excess of alkali (NaOH) in the NaClO solution, the nitrogen remains unabsorbed, and is collected, and measured in a tube graduated in cubic inches.

The volume of nitrogen is corrected for temperature (60°F.) and barometric pressure (30 inches), and the quantity of urea calculated from the volume of nitrogen obtained.



1 molecule (60) of urea contains two atoms ($2 \times 14 = 28$) of nitrogen.

28 grains N = 93.33 cubic inches.

60 grains urea contain 28 grains N = 93.33 cubic inches nitrogen, at temperature of 60°F. and barometric pressure of 30 inches.

Grains urea.	Grain urea.	Cubic inches.	Nitrogen.
60	: 1	:: 93.33	: 1.55 cu. in.

Consequently 1.55 cubic inches nitrogen are evolved from 1 grain urea, or 1 cubic inch of nitrogen is evolved from 0.645 grain of urea.

Nitrogen.	Cu. in. N.	Grain urea.	Urea.
1.55	: 1	:: 1	: 0.645 grain.

Method: Fill one-third of the tube, graduated in cubic inches, with mercury, add 100 grains urine, and rapidly fill the remainder of the tube with sodium hypochlorite solution. Quickly place the thumb over the opening of the tube and invert it in a mercury-trough. Decomposition of the urea will occur, and the evolved nitrogen will collect in the upper part of the tube.

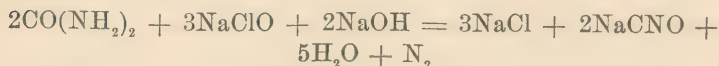
After the lapse of about half an hour close the opening of the tube with the thumb and transfer it to a vessel of water. Equalize the atmospheric pressure, and read off the number of cubic inches of nitrogen evolved. Divide the number of cubic inches nitrogen evolved by 1.55 or multiply by 0.645, and the result will be the percentage of urea (100 grains of urine having been employed).

Suppose 4.65 cubic inches nitrogen evolved.

$$4.65 \div 1.55 = 3 \text{ per cent. urea.}$$

Or, $4.65 \times 0.645 = 2.99$ per cent. (3 per cent.) urea.

Objections to this method: According to Fenton, NaClO in presence of caustic alkalies causes the evolution of only one-half of the nitrogen of urea, the remainder being retained as cyanate, thus:



2. *Fowler's modification of Davy's method* for the estimation of urea: Depends upon the decomposition of urea in solution by sodium hypochlorite (NaClO), thereby causing a reduction in the density of the solution. Fowler found that a loss of one degree in specific gravity in a mixture of one volume of urine and seven volumes of hypochlorite solution represented the presence (decomposition) of 0.77 per cent. of urea.

Seven volumes of hypochlorite solution of 1035 specific gravity will decompose the urea in one volume of an average urine.

Method: Determine the specific gravity of the urine and of the hypochlorite solution separately. To one volume of the urine add seven volumes of hypochlorite solution, say 10 c.c. urine to 70 c.c. hypochlorite. (The specific gravity of this mixture is determined by calculation.) Allow to stand until the decomposition is completed (about half an hour), then determine the specific gravity of the resulting liquid, and deduct this specific gravity from the specific gravity of the mixture obtained by calculation.

Example:

7 volumes of NaClO sol., specific gravity $1036 \times 7 = 7252$

1 volume of urine, " " $1025 \times 1 = 1025$

8 volumes 8)8277

Specific gravity of mixture before decomposition, 1034.6

" " " after " 1030.0

Hence 4.6

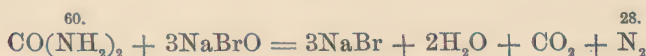
$$4.6 \times 0.77 = 3.524 \text{ per cent. urea.}$$

This method does not furnish accurate results.

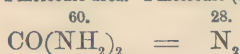
3. *Hypobromite method* for estimating urea: Depends upon the decomposition of the urea in the urine by means of sodium hypobromite (NaBrO) with the production of sodium bromide (NaBr), water, carbon dioxide (CO₂), and the evolution of nitrogen.

The CO_2 is absorbed by the excess of alkali (NaOH) in the NaBrO solution, and the nitrogen remains unabsorbed, and is collected, and measured in a tube graduated in cubic centimetres.

The volume of nitrogen is corrected for temperature (0°C.) and barometric pressure (760 mm.), and the quantity of urea calculated from the volume of nitrogen obtained.



1 molecule urea. 1 molecule (2 atoms).



60 grammes of urea contain 28 grammes nitrogen.

28 grammes nitrogen = 22.32 litres or 22320 c.c.

60 grammes urea evolve 22.32 " " 22320 c.c. nitrogen.

Grms. urea.	Grm. urea.	Litres.	Litre.
60 :	1 ::	22.32 :	0.372 or 372 cubic centimetres.

1 gramme of urea will evolve 372 c.c. of nitrogen (at 0°C. and 760 mm.)

c.c. N.	c.c. N.	Grm. N.	Grm. N.
372 :	1 ::	1 :	0.002688

1 cubic centimetre of nitrogen, measured at 0°C. temperature and 760 mm. pressure, is evolved from 0.002688 grm. urea (2.688 milligrammes urea).

1.0 gramme urea evolves 372.0 c.c. nitrogen.

0.001 " " " 0.372 " "

0.010 " " " 3.72 " "

0.020 " " " 7.44 " "

0.030 " " " 11.16 " "

1 c.c. of a 1 per cent. solution of urea (containing 0.010 urea) will evolve 3.72 c.c. nitrogen.

1 c.c. of a 2 per cent. solution of urea (containing 0.020 urea) will evolve 7.44 c.c. nitrogen.

The *sodium hypobromite solution* is prepared by dissolving 100 grammes sodium hydroxide (NaOH) in 250 c.c. water, cooling the solution, and adding 25 c.c. (75 grammes) of bromine.

The reagent (NaBrO solution) should be freshly prepared.



$$\begin{array}{cccc} 2\text{Br.} & 2\text{NaOH.} & \text{Grm. Br.} & \text{NaOH.} \\ 160 & : 80 & :: 75 & : 37.5 \text{ grm.} \end{array}$$

Hence the 75 grammes of bromine will combine with only 37.5 grammes of the 100 grammes of NaOH employed in the preparation of the solution, leaving the difference between 37.5 and 100, or 62.5 grammes, free NaOH in the solution, to absorb the CO_2 evolved in the application of the method.

There are many forms of apparatus employed in the estimation of urea by sodium hypobromite,—

Russell & West's.

Huefner's.

Greene's.

Marshall's.

Etc.

Method, with the use of Marshall's apparatus: Close the side opening of the bulbed tube with the thumb and fill with hypobromite solution (which may previously be diluted with an equal volume of distilled water). Close the upper opening with a rubber stopper and incline the tube so as to allow any air-bubbles which may be just below the rubber stopper to escape through the side opening. Invert the tube, and fix the end closed with the rubber stopper in the saucer-shaped vessel.

Slowly run 1 c.c. of the urine, from the graduated pipette, into the hypobromite solution through the side opening, and quickly withdraw the pipette.

1 c.c. of urine, in the great majority of cases, suffices; if, however, the urine contain very little urea, more than 1 c.c. may be employed.

When the decomposition is completed (about twenty minutes) and all the gas-bubbles have collected in the upper part of the tube (may be facilitated by gently tapping the tube with the finger), equalize the atmospheric pressure by attaching the funnel-tube to the side opening of the hypobromite tube, and pour hypobromite solution into it until the surfaces of the liquid in both tubes are equal in height. Read off the number of cubic centimetres of nitrogen, the temperature of the air, and the barometric pressure.

Suppose 1 c.c. urine evolved 12.5 c.c. nitrogen, the temperature being 20°C . and barometric pressure 750 mm.

A. Then, correcting simply for temperature and pressure,

$$\begin{array}{ccc} 20^{\circ}. & 0^{\circ}. & 20^{\circ}. \\ a. & 293 : 273 :: 12.5 : 11.64 \text{ c.c. at } 0^{\circ} \text{ C. temp.} \end{array}$$

and,

$$b. \quad 760 : 750 :: 11.64 : 11.48 \text{ c.c. at } 0^{\circ} \text{ C. temp. and } 760 \text{ mm.}$$

Hence

$$11.48 \text{ c.c. N} \times 0.002688 = 0.03085 \text{ urea (in 1 c.c. urine).}$$

$$0.03085 \times 100 = 3.085 \text{ per cent. urea (in 100 c.c. urine).}$$

B. Correcting for temperature, barometric pressure, and tension of aqueous vapor,

$$V' = \frac{v \times (B-T)}{760 \times (1 + 0.003665 t)}$$

in which

V' is the corrected volume of nitrogen in c.c.

v " observed " " "

B " barometric pressure in mm.

T " tension of aqueous vapor for temp. t .

t " observed temperature.

0.003665 is the coefficient of expansion of gases for each degree Centigrade.

Hence, for the above example (A),

$$\frac{12.5 \times (750 - 17.4)}{760 \times 1.073} = \frac{12.5 \times 732.6}{760 \times 1.073} = \frac{9157.50}{815.48} = 11.23 \text{ c.c. N}$$

$$11.23 \text{ c.c. N} \times 0.002688 = 0.03018 \text{ (in 1 c.c. urine).}$$

$$0.03018 \times 100 = 3.018 \text{ per cent. urea (in 100 c.c. urine).}$$

In example A, correcting for tension of aqueous vapor,

$$(750 - 17.4)$$

$$760 : 732.6 :: 11.64 : 11.23 \text{ c.c. nitrogen.}$$

$$11.23 \text{ c.c. N} \times 0.002688 = 0.03018 \text{ urea (in 1 c.c. urine).}$$

$$0.03018 \times 100 = 3.018 \text{ per cent. urea (in 100 c.c. urine).}$$

C. To correct for the expansion of mercury at 20° C. in the barometer-tube,

$$0.000171 \times t^{\circ}$$

thus,

$$0.000171 \times 20 = 0.0034$$

$$0.0034 \times 750 = 2.56 \text{ mm.}$$

so,

$$B = 750 - 2.56 = 747.44.$$

$$747.44 - 17.4 \text{ (tension of aq. vapor for } 20^{\circ} \text{ C.)} = 730.04.$$

$$750 : 730.04 :: 11.23 : 10.93 \text{ c.c. N.}$$

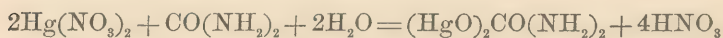
$$10.93 \text{ c.c.} \times 0.002688 = 0.02937 \text{ grm. urea.}$$

$$0.02937 \times 100 = 2.937 \text{ per cent. urea (in 100 c.c. urine).}$$

TABLE OF TENSION OF AQUEOUS VAPOR EXPRESSED IN MILLI-METRES FOR CERTAIN TEMPERATURES CENTIGRADE.

Temp.	Tension in mm.	Temp.	Tension in mm.
10° C. . . .	9.165	18° C. . . .	15.357
11° C. . . .	9.792	19° C. . . .	16.346
12° C. . . .	10.457	20° C. . . .	17.391
13° C. . . .	11.162	21° C. . . .	18.495
14° C. . . .	11.908	22° C. . . .	19.659
15° C. . . .	12.699	23° C. . . .	20.888
16° C. . . .	13.536	24° C. . . .	22.184
17° C. . . .	14.421	25° C. . . .	23.550

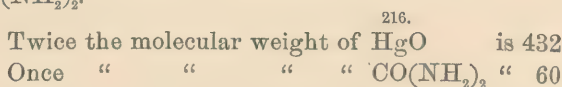
4. *Liebig's Method* for the estimation of urea: Depends upon the production of an insoluble compound of mercuric oxide and urea $(\text{HgO})_2\text{CO}(\text{NH}_2)_2$ on the addition of mercuric nitrate $\text{Hg}(\text{NO}_3)_2$ to a solution of urea.



In the practical application of the method the $\text{Hg}(\text{NO}_3)_2$ acts first on the NaCl of the urine to form soluble HgCl_2 . When sufficient has been added to combine with all the NaCl present it then acts on the urea.



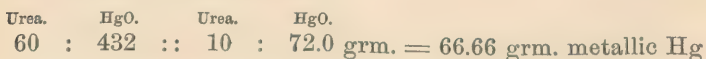
The precipitate formed after the NaCl is satisfied is composed of 2 molecules of HgO in combination with 1 molecule of $\text{CO}(\text{NH}_2)_2$.



In the formation of the compound $(\text{HgO})_2\text{CO}(\text{NH}_2)_2$, 432 parts by weight of HgO enter into combination with 60 parts by weight of $\text{CO}(\text{NH}_2)_2$.

PREPARATION OF STANDARD SOLUTION.

The quantity of HgO necessary to prepare 1000 c.c. of standard $\text{Hg}(\text{NO}_3)_2$ solution so that 1 c.c. of it shall equal 0.010 urea, is determined by



In the preparation of the solution 5.2 grm. HgO must be added to the 72.0 grm. to act on the indicator.

$72.0 + 5.2 = 77.2$ gm. $\text{HgO} = 71.48$ gm. metallic Hg.

Hence 1000 c.c. containing 77.2 gm. $\text{HgO} = 10.0$ gm. urea.
 1 c.c. " 0.0772 " " = 0.010 " "

This same solution may be used for the estimation of sodium chloride.

HgO.	2NaCl.	HgO.	NaCl.
216	: 117	:: 77.2	: 41.817 gm.

1000 c.c. containing 77.2 gm. HgO	$=$	$\overset{\text{NaCl.}}{41.817}$	gm.
1 c.c. " " " "	$=$	0.041879	"

The insoluble HgO , or the metallic Hg, is converted into soluble $\text{Hg}(\text{NO}_3)_2$ by dissolving in nitric acid.

Dissolve 77.2 gm. HgO or 71.48 gm. metallic Hg with nitric acid and a little water, evaporate excess of acid, and dissolve the residue with distilled water, dilute slowly to 1000 c.c. If on dilution with water a canary-yellow precipitate of basic mercuric nitrate should separate, allow it to subside, pour off and preserve the supernatant liquid, dissolve the precipitate with a few drops strong nitric acid, and return the previously poured off supernatant liquid to the original vessel.

The mercuric nitrate solution must be standardized with a standard solution of urea of 2 per cent. strength.

PREPARATION OF THE STANDARD UREA SOLUTION.

Dissolve 2.0 gm. dry urea in distilled water and dilute to 100 c.c.

	Urea.
100 c.c.	$= 2.0$ gm.
10 c.c.	$= 0.200$ "
1 c.c.	$= 0.020$ "

The indicator is a strong solution of sodium carbonate. With mercuric nitrate it produces yellowish-brown basic mercuric oxycarbonate, $\text{HgCO}_3(\text{HgO})_3$.



To standardize the mercuric nitrate solution, place 10 c.c. of the standard urea solution ($= 0.200$ urea) in a beaker, and run the mercuric nitrate solution into it from a burette, stirring after each addition, until a drop of the liquid in the beaker produces a slight yellow color when brought, by means of a glass rod, in contact with sodium carbonate solution on a porcelain tablet.

If 1 c.c. of the mercuric nitrate solution is equal to 0.01 urea, then 20 c.c. should be required to combine with the urea (0.200) present in the 10 c.c. urea solution and act on the indicator.

1000 c.c.	contains	5.2	gram.	HgO	to act on the indicator.
1 c.c.	"	0.0052	"	"	"

20 c.c. HgO solution having been required for the 10 c.c. urea solution, and as each c.c. HgO solution contains 0.0052 HgO to act on the indicator, 20×0.0052 or 0.104 HgO must have been added with the 20 c.c. HgO solution to the 10 c.c. urea solution. Hence, in the combined volumes, 20 c.c. + 10 c.c. = 30 c.c., there were present 0.104 HgO, and in each c.c. $0.104 \div 30 = 0.003466$ HgO to act on the indicator.

If a larger or smaller quantity than 20 c.c. should be required, the mercuric nitrate solution must be corrected after the manner given for solutions too strong or too weak in the correction of the argentic nitrate solution for the estimation of sodium chloride.

The phosphates, sulphates, and carbonates in the urine interfere with the application of the method. They are removed by the baryta mixture, composed of

2 volumes of a cold saturated solution of barium hydroxide ($\text{Ba}(\text{OH})_2$).

1 volume of a cold saturated solution of barium nitrate ($\text{Ba}(\text{NO}_3)_2$).

Method: Mix 40 c.c. urine with 20 c.c. baryta mixture, filter through a dry filter, neutralize the filtrate with a drop or two of nitric acid. With a pipette transfer 15 c.c. of the filtrate (representing 10 c.c. urine and 5 c.c. baryta mixture) to a beaker, and slowly run the mercuric nitrate solution into it from a burette, stirring after each addition, until a permanent milky turbidity is produced (action on the urea). The quantity of mercuric nitrate solution added up to this point was required by the sodium chloride.

Note the number of c.c. mercuric nitrate solution added, multiply by 0.0418, and the result will represent the quantity of sodium chloride in 10 c.c. of the urine, and this, multiplied by 10, gives the percentage.

Continue the addition of the mercuric nitrate solution, stirring after each addition, until a drop of the liquid in the

beaker produces a slight yellow color when brought, by means of a glass rod, in contact with the indicator (sodium carbonate) on a porcelain tablet.

Read off the total number of c.c. mercuric nitrate solution required for the sodium chloride and urea. Deduct from this number the quantity required for the sodium chloride, and the remainder will be the quantity required for the urea. If *more than 30 c.c.* of mercuric nitrate solution have been required for the urea alone, then *for every 4 c.c. required over 30 c.c. add 0.1 c.c.* to the number of c.c. required.

If *less than 30 c.c.* of mercuric nitrate solution have been required for the urea alone, then *for every 4 c.c. required less than 30 c.c. deduct 0.1 c.c.* from the number of c.c. required.

Then multiply the corrected number of c.c. mercuric nitrate solution by 0.010, and the result will represent the quantity of urea in 10 c.c. of the urine, and this, multiplied by 10, gives the percentage.

Suppose a total quantity of 36 c.c. mercuric nitrate solution had been required,

$$\begin{array}{r} 36 \text{ c.c.} \\ \underline{2 \text{ c.c. for NaCl.}} \\ 34 \text{ c.c. for urea.} \\ \underline{30} \\ 4 \text{ (once 4 over 30).} \end{array}$$

Hence $34.0 \text{ c.c.} + 0.1 = 34.1 \text{ c.c.}$
 $34.1 \times 0.010 = 0.341 \text{ grm.}$
 $0.341 \times 10 = 3.41 \text{ per cent. urea.}$

These corrections are necessary to make the results correspond to the end reaction obtained in standardizing the mercuric nitrate solution, in which there were just two volumes of the mercuric nitrate solution employed for one volume of the urea solution.

Examples :

1. Take 10 c.c. of 2 per cent. *urea solution*, and add to it 20 c.c. of the HgO solution. We have in each c.c. of the HgO solution 5.2 milligrammes of HgO in excess to act on the indicator. In 20 c.c. we have $5.2 \times 20 = 104$ milligrammes excess of HgO in the 30 c.c. Therefore in each c.c. of this 30 c.c. solution we have $104 \div 30$ or 3.466 milligrammes of HgO in excess to act on the indicator.

2. 10 c.c. of *urine* containing 3 per cent. of urea, plus 5 c.c. of *baryta mixture*, plus 30 c.c. of HgO solution. In each c.c.

of HgO solution we have 5.2 milligrammes excess of HgO. In 30 c.c. we have 30×5.2 milligrammes = 156 milligrammes excess in 45 c.c. mixture. Therefore in 1 c.c. we have $156 \div 45 = 3.466$.

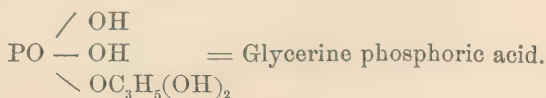
3. 10 c.c. of *urine* containing 4 per cent. of urea, plus 5 c.c. of *baryta mixture*, plus 40 c.c. of HgO solution. In 40 c.c. of HgO solution we have $40 \times 5.2 = 208$ milligrammes excess of HgO in 55 c.c. mixture. Therefore in 1 c.c. we have $208 \div 55 = 3.781$. But adding 5 c.c. of H₂O to the mixture, we have 208 milligrammes of HgO excess in 60 c.c. mixture, and, therefore, in 1 c.c. we have $208 \div 60 = 3.466$.

4. 10 c.c. of *urine* containing 2 per cent. of urea, plus 5 c.c. of *baryta mixture*, plus 20 c.c. of HgO solution. In 20 c.c. of HgO solution we have 5.2×20 or 104 milligrammes of HgO excess in 35 c.c. of mixture. Therefore in each c.c. we have $104 \div 35 = 2.971$. But 10 c.c. of a 2 per cent. urea solution plus 5 c.c. of *baryta mixture* will require 20.23 c.c. of HgO. In 20 c.c. of HgO solution we have $20 \times 5.2 = 104$ milligrammes in excess. Each c.c. of the standard solution of HgO contains 77.2 milligrammes of HgO, therefore 0.23 c.c. will contain $77.2 \times 0.23 = 17.75$ in excess, plus $104 = 121.75 \div 35.23 = 3.466$ c.c.

PHOSPHORIC ACID.

Phosphoric acid occurs in the urine partly in combination with sodium, potassium, and ammonium (alkaline phosphates), and partly with calcium and magnesium (earthy phosphates).

It also occurs in small quantity in the urine as glycerine phosphoric acid (C₃H₅PO₆).



About four-fifths of the phosphoric acid in the urine is in combination as alkaline phosphates, and one-fifth as earthy phosphates.

Phosphoric acid in the urine is estimated in terms of P₂O₅ (phosphoric anhydride).

The volumetric method for the estimation of *phosphoric acid* in the urine depends upon the principle that P₂O₅ in the presence of free acetic acid and an acetate of an alkali, on the application of heat, is precipitated by uranium acetate or nitrate as insoluble (UrO₃)₂P₂O₅.

It is always necessary to standardize the uranium solution with a standard solution of P_2O_5 .

The standard solution of P_2O_5 is prepared so that it shall contain 0.2 per cent. P_2O_5 .

1. *Preparation of standard solution of P_2O_5 .*

Di-sodic hydrogen phosphate ($Na_2HPO_4 + 12H_2O$) is selected for this purpose.

Two molecules of $Na_2HPO_4 + 12H_2O$ contain one molecule of P_2O_5 .

$$\begin{array}{rcl} Na_2HPO_4 + 12H_2O & = & 358 \times 2 = 716 \\ P_2O_5 & & = 142 \end{array}$$

Hence to determine the quantity of $Na_2HPO_4 + 12H_2O$ necessary to prepare 1000 c.c. solution, so that it shall contain 2 gm. P_2O_5 (0.2 per cent.),

$$\begin{array}{ccccccc} P_2O_5. & 2Na_2HPO_4 + 12H_2O. & P_2O_5. & Na_2HPO_4 + 12H_2O. \\ 142 & : & 716 & :: & 2 & : & 10.085 \text{ gm.} \end{array}$$

or to prepare only 250 c.c. of the standard $Na_2HPO_4 + 12H_2O$ solution,

$$\begin{array}{ccccccc} & & Na_2HPO_4 + 12H_2O. \\ 142 & : & 716 & :: & 0.5 & : & 2.521 \text{ gm.} \end{array}$$

Dissolve 10.085 gm. pure non-effloresced *di-sodic hydrogen phosphate* in water and dilute to 1000 c.c., or to prepare only 250 c.c. of the solution, dissolve 2.521 gm. of the phosphate in water and dilute to 250 c.c.

$$\begin{array}{rcl} & P_2O_5. & \\ 1000 \text{ c.c.} & = & 2.000 \text{ gm.} \\ 100 \text{ c.c.} & = & 0.200 \text{ " } \\ 50 \text{ c.c.} & = & 0.100 \text{ " } \\ 1 \text{ c.c.} & = & 0.002 \text{ " } \end{array}$$

2. *Preparation of uranium acetate, or nitrate solution.*

The precipitate formed when uranium acetate, or nitrate, is added to a solution containing P_2O_5 is $(UO_3)_2P_2O_5$,—i.e., two molecules of UO_3 in combination with one molecule of P_2O_5 .

$$\begin{array}{rcl} & 288. & \\ \text{Twice the molecular weight of } UO_3 & \text{is} & 576 \end{array}$$

$$\begin{array}{rcl} & 142. & \\ \text{Once " " " " } P_2O_5 & \text{" } & 142 \end{array}$$

The quantity of uranium oxide (UO_3) required to prepare 1000 c.c. of standard solution so that 1 c.c. shall equal 0.010 P_2O_5 is determined:

$$\begin{array}{rcl} P_2O_5. & 2UO_3. & P_2O_5. & UO_3. \\ 142 : 576 & :: & 10 : 40.56 \text{ gm.} = \text{to } 10 \text{ gm. } P_2O_5 \end{array}$$

The quantity of uranium acetate ($\text{UO}_3(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{H}_2\text{O}$) or of the nitrate ($\text{UO}_3\text{N}_2\text{O}_5 + 6\text{H}_2\text{O}$) equivalent to 40.56 grm. UO_3 is determined:

UO_3 .	Uran. acetate.	UO_3 .	Uran. acetate.
288	: 442	:: 40.56	: 62.24 grm.
UO_3 .	Uran. nitrate.	UO_3 .	Uran. nitrate.
288	: 504	:: 40.56	: 70.98 grm.

The quantities of uranium acetate and of nitrate necessary to prepare 1000 c.c. of solution may also be calculated by one proportion:

P_2O_5 .	2 Uran. acetate.	P_2O_5 .	Uran. acetate.
142	: 884	:: 10	: 62.24 grm.
P_2O_5 .	2 Uran. nitrate.	P_2O_5 .	Uran. nitrate.
142	: 1008	:: 10	: 70.98 grm.

Because of uranium acetate and nitrate being contaminated with oxides of uranium the respective quantities, as indicated by the above proportions, are dissolved in 900 c.c. water instead of 1000 c.c.

Ammonium salts in the urine interfere with uranium nitrate, therefore uranium acetate is preferred in the preparation of the standard solution.

Boil 62.2 grm. *uranium acetate* or 70.98 grm. *uranium nitrate* with about 850 c.c. water, allow to cool, filter off the insoluble oxides of uranium, and dilute to 900 c.c.

3. *Preparation of the solution containing an acetate of an alkali and free acetic acid.*

Dissolve 50 grm. *sodium acetate* in 450 c.c. water, and add *acetic acid* until the volume reaches 500 c.c.

4. The *indicator* is a solution of *potassium ferrocyanide* of about ten per cent. strength. With a soluble uranium salt it produces a chocolate color (due to formation of uranium ferrocyanide).

To *standardize the uranium acetate solution*, place 50 c.c. of the standard phosphoric acid solution (containing 0.100 grm. P_2O_5) in a beaker, add 5 c.c. of the acetate of an alkali solution, and heat the liquid to the simmering-point. Slowly run the uranium acetate solution (about one-half c.c. at a time) into it from a burette, stirring after each addition, until a drop of the liquid in the beaker produces a *slight chocolate color* when brought, by means of a glass rod, in contact with the potassium ferrocyanide solution on a porcelain tablet.

Note the number of cubic centimetres uranium solution required.

Suppose 8 c.c. of uranium solution were required. The solution is too strong and must be diluted. For every 8 c.c. of the uranium solution (of the 900 c.c.) remaining add a volume of water equal to the difference between 8 and 10, or 2 c.c.

900 c.c. original volume of solution.

8 c.c. volume used.

8) 892 c.c. volume remaining.

$111.5 \times 2 = 223$ c.c. water to be added to the 892 c.c. uranium solution.

10 c.c. will now equal $\overset{\text{P}_2\text{O}_5}{0.100}$ grm.

1 c.c. " " " 0.010 "

Method: Place 50 c.c. urine in a beaker, add 5 c.c. acetate of an alkali solution, and heat the liquid to the simmering-point. Slowly run the uranium acetate solution (about one half c.c. or less at a time) into it from a burette, stirring after each addition, until a drop of the liquid in the beaker produces a *slight* chocolate color when brought, by means of a glass rod, in contact with the potassium ferrocyanide solution on a porcelain tablet.

The first titration (adding about 0.5 c.c. at a time) usually gives only approximate results, unless performed with great care. A second titration should be made, and the uranium solution slowly run in until within 0.5 c.c. of the quantity required in the first titration. Continue the addition of the uranium solution, 0.1 c.c. at a time, testing with the indicator after each addition, until a slight chocolate color is obtained.

Read off the number of cubic centimetres uranium acetate solution required and multiply this number by 0.010, and the result will represent the quantity of P_2O_5 in 50 c.c. urine.

Multiply this result by 2 to obtain the percentage.

Suppose 8.6 c.c. uranium solution were required.

Then

$$8.6 \times 0.010 = 0.086 \times 2 = 0.172 \text{ per cent. } \text{P}_2\text{O}_5 \text{ (total).}$$

ESTIMATION OF THE EARTHY PHOSPHATES IN URINE.

To 200 c.c. urine add excess of ammonium hydroxide (NH_4OH) (about 10 c.c. ordinary strength NH_4OH), and

allow to stand twelve hours. Collect the precipitated earthy phosphates (phosphates of calcium and magnesium) on a filter, and wash several times with water containing a few drops NH_4OH . Place a beaker with a 50 c.c. mark on it under the funnel. Pierce the filter with a glass rod, and treat the precipitate drop by drop with about 3 or 4 c.c. acetic acid. This is to dissolve the earthy phosphates. Wash the remainder of the precipitate with water into the beaker below until 50 c.c. liquid are collected.

Add 5 c.c. of acetate of alkali solution and heat the liquid to the simmering-point.

Slowly run the uranium acetate solution (less than one-half c.c. at a time) into it, stirring after each addition until a drop of the liquid in the beaker produces a *slight* chocolate color when brought, by means of a glass rod, in contact with the potassium ferrocyanide solution on a porcelain tablet.

Multiply the number of cubic centimetres uranium acetate solution required by 0.010, and divide the result by 2, this will represent the percentage of P_2O_5 in combination with the alkaline earths.

Suppose 5.4 c.c. uranium acetate solution were required.

$$5.4 \times 0.010 = 0.054 \div 2 = 0.027 \text{ per cent. of } \text{P}_2\text{O}_5.$$

Deduct the percentage of earthy phosphates from the total phosphates, and the remainder is the quantity of P_2O_5 in combination with the alkalis.

Suppose the percentage of total $\text{P}_2\text{O}_5 = 0.172$ per cent.

$$\begin{array}{rcccccl} \text{"} & \text{"} & \text{"} & \text{"} & \text{earthy} & \text{"} & = & 0.027 & \text{"} \\ \text{"} & \text{"} & \text{"} & \text{"} & \text{alkaline} & \text{"} & = & 0.145 & \text{"} \end{array}$$

Phosphoric acid often occurs in urinary sediments as triple phosphate (magnesium ammonium phosphate, MgNH_4PO_4).

Phosphoric acid may occur in combination in the form of urinary calculi. It does not occur as frequently as uric acid calculi.

PHOSPHATIC CALCULI MAY OCCUR IN THREE FORMS.

1. *Composed of calcium phosphate.*

Three varieties,—acid, neutral, and basic.

- a. $\text{Ca}_3(\text{PO}_4)_2$
- b. $\text{CaH}_4(\text{PO}_4)_2$
- c. CaHPO_4

All soluble in nitric acid; when their solution is neutralized with NH_4OH they are reprecipitated.

Heat does not affect them.

2. *Composed of magnesium ammonium phosphate* (MgNH_4PO_4). Triple phosphate most common form.

Soluble in hydrochloric acid. When the hydrochloric acid solution is neutralized with NH_4OH , crystalline triple phosphate appears. When heated, ammoniacal gas is evolved.

3. *Fusible phosphates usually composed of 1 and 2 (above)*. Contain more or less organic matter.

URIC ACID OR LITHIC ACID. $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$.

Molecular weight, 168.

A dibasic acid,—*i.e.*, contains two replaceable atoms of hydrogen, $\text{H}_2\text{C}_5\text{H}_2\text{N}_4\text{O}_3$.

Found in urine chiefly as sodium acid urate, $\text{NaHC}_5\text{H}_2\text{N}_4\text{O}_3$.

Present from 0.2 part to 1.0 part in 1000 parts urine.

Average percentage in urine 0.05 per cent.

Recognized as a distinct compound by Scheele in 1776. Studied more fully by Liebig in 1838. Was prepared synthetically in 1882.

Formerly called lithic acid.

It is contained in the solid excrement of birds and serpents, from which source it is most readily obtained by treating the excrement with a 5 per cent. solution of NaOH , filtering, and adding HCl to the filtrate. The uric acid is precipitated in an amorphous state or, on standing, may separate in crystalline form.

It may be deposited in the joints, as in the uric acid diathesis (gout).

QUANTITATIVE ESTIMATION OF URIC ACID.

If albumen be present, remove by coagulation by heat. To 200 c.c. urine (if not clear, filter) add 5 or 10 c.c. HCl , and allow to stand about twenty-four hours. Uric acid separates in crystalline form. Some of the crystals float on the surface of the liquid.

Collect the crystals on a washed or on an equipoised filter, using the filtrate to wash the crystals out of the beaker. Wash the crystals with small portions of water (5 c.c.) at a time until the filtrate is free from hydrochloric acid (test with AgNO_3 solution).

Allow the crystals to dry on the filter, separate the two equipoised filters, and weigh.

The weight obtained is the quantity of uric acid in 200 c.c. urine. Divide the weight by 2, and the result is the percentage.

If over 30 c.c. of water are required in the washing, then for every cubic centimetre of water employed over 30 c.c. 0.000045 grm. must be added to the weight of uric acid obtained. (1 c.c. water applied in this manner dissolves 0.000045 grm. uric acid.)

No correction is necessary when only 30 c.c. are required in the washing.

The uric acid in crystallizing takes up coloring-matter from the urine, but the amount of uric acid dissolved by the 30 c.c. water used in washing is just sufficient to compensate for the increase of weight due to the coloring-matter taken up.

To obtain the crystals pure and colorless, dissolve them in about 75 c.c. water to which about 1 c.c. of a 10 per cent. solution of NaOH has been added. Acidulate the solution with HCl, and allow to stand twenty-four hours. Uric acid will separate. If not colorless, collect it on a filter, redissolve in water with the aid of NaOH, and add HCl as before, and repeat the operation, if necessary, until colorless crystals are obtained.

Uric acid crystallizes in many forms, most often in wedge-shaped crystals.

It is soluble in 15,000 parts cold and 2000 parts hot water. Insoluble in alcohol and ether. Soluble in an alkaline solution and in sulphuric acid. Insoluble in hydrochloric acid.

When burned, an odor similar to burnt feathers is produced. Is dibasic; forms neutral and acid salts.

Neutral salts:

- a. $K_2C_5H_2N_4O_3$, soluble in 44 parts cold water.
- b. $Na_2C_5H_2N_4O_3$, less soluble than the corresponding potassium salt.
- c. The ammonium salt is not known.

Acid salts:

- a. $KHC_5H_2N_4O_3$, soluble in 800 parts water.
- b. $NaHC_5H_2N_4O_3$, less soluble than the corresponding potassium salt.
- c. $NH_4HC_5H_2N_4O_3$, soluble in 1800 parts water.

Uric acid treated with *cold strong nitric acid* (specific gravity 1.41) is oxidized, with the formation of *alloxan* ($C_4H_2N_2O_4$). Effervescence occurs, and urea is produced at the same time.



Uric acid treated with *hot dilute nitric acid* is oxidized, with the formation of *alloxantin* ($C_8H_4N_4O_7$).

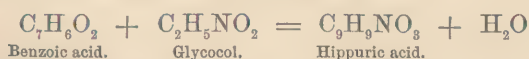
TESTS FOR URIC ACID.

1. *Murexide test*: Place the solid uric acid, or evaporate its solution to dryness, in a small dish, cover the uric acid with strong nitric acid, and evaporate to dryness on a water-bath. Allow to cool, and moisten the residue with a drop of very dilute ammonium hydroxide. A beautiful red color will appear, due to the formation of murexide (ammonium purpurate, $C_8H_8N_6O_6 = NH_4C_8H_4N_5O_6$).

2. *Schiff's test*: Dissolve the uric acid in a solution of sodium carbonate, and bring a drop of the solution in contact with filter-paper which had been previously saturated with a solution of argentic nitrate. Spots of reduced silver of a yellowish-brown or deep-black color, depending upon the quantity of uric acid in the solution, will appear.

Hippuric acid ($C_9H_9NO_3$) is contained in very small quantity in human urine.

Benzoic acid ($C_7H_6O_2$) taken into the human organism is converted into hippuric acid through the agency of glyocol ($C_2H_5NO_2$), a body formed in the liver, thus:



Quinic acid ($C_7H_{12}O_6$), one of the acids contained in cinchona bark, and also in coffee-beans, is eliminated as hippuric acid. Hippuric acid appears in the urine after eating cranberries.

CREATININE. $C_4H_7N_3O$. Molecular weight, 113.

First recognized in 1844. Isolated by Liebig in 1847.

Occurs in the urine of man (0.06 per cent.), horse, cow, sheep, and dog.

A substance supposed to be creatinine was found in muscle, but was afterwards shown to be creatine ($C_4H_9N_3O_2$).

Creatinine crystallizes in colorless prisms. Soluble in 12 parts water and in 100 parts alcohol.

Its solution is strongly alkaline. Will change red litmus to blue, and will brown turmeric paper. Has a caustic taste, somewhat like dilute ammonium hydroxide. Is the strongest of all bases of animal origin.

It unites with acids, without displacing the hydrogen in the acid, to form salts, as



It combines with one molecule of water to form creatine:



It combines with zinc chloride to form creatinine zinc chloride, $(\text{C}_4\text{H}_7\text{N}_3\text{O})_2\text{ZnCl}_2$, which contains 62.432 per cent. of creatinine.

QUALITATIVE TESTS FOR CREATININE.

1. A solution of creatinine treated with a few drops sodium hydroxide and a little picric acid and warmed is colored claret-red.

2. *Weyl's test*: If a dilute creatinine solution be treated with a few drops of *very* dilute sodium nitroprusside solution, and then a dilute solution of sodium hydroxide be added drop by drop, the liquid becomes ruby-red in color, changing in a few moments to an intense straw color, which in turn becomes green when warmed with acetic acid.

Creatinine reduces Fehling's solution. The blue liquid is changed to yellow. The cuprous oxide does not separate, but remains in solution.

QUANTITATIVE ESTIMATION OF CREATININE IN URINE.

Treat 300 c.c. urine with milk of lime until slightly alkaline, and add solution of calcium chloride as long as a precipitate forms (may require 5 to 8 c.c. CaCl_2 solution). Filter, and evaporate filtrate to syrup-like consistence (to about 20 c.c.) on a water-bath, and while warm add about 50 c.c. alcohol (95 per cent.).

Stir the liquid with a glass rod until a precipitate is formed. (The precipitate may form only after long stirring.) Filter, and wash the dish and the filter with about 10 c.c. alcohol (in 2 or 3 portions), collecting the wash-alcohol with the filtrate. (The precipitate may be thrown away.) Cover the beaker containing the filtrate, and allow it to stand twenty-four hours.

If a precipitate should separate after standing twenty-four hours, filter through a small filter and wash with about 10 c.c. alcohol (in 2 or 3 portions), and collect the washings with the filtrate.

Concentrate the filtrate by evaporation to about 60 c.c., and when cold add 1 c.c. of acid free zinc chloride solution of 1.2 specific gravity.

Stir the liquid until a precipitate (cloudiness) begins to form. (The precipitate may form only after long stirring.) Cover the beaker, and allow to stand two or three days.

Creatinine zinc chloride separates in crystalline tufts or rosettes.

Collect the precipitate of creatinine zinc chloride on an equipoised filter (using the filtrate, if necessary, to transfer the precipitate from the beaker).

Wash the precipitate with alcohol (2 or 3 c.c. at a time) until the filtrate is colorless and free from chlorine (test with AgNO_3). Dry the precipitate on the filter at a temperature of 100°C . and, when dry, weigh.

Every 100 parts $(\text{C}_4\text{H}_7\text{N}_3\text{O})_2\text{ZnCl}_2$ contain 62.432 parts creatinine.

Then,

$100 : 62.432 :: \text{weight of precipitate} : x = \text{quantity of creatinine in the 300 c.c. urine employed.}$

Divide this by 3 to obtain the percentage.

The creatinine may be obtained from the creatinine zinc chloride by dissolving the latter in hot water and boiling it from one-quarter to one-half hour with freshly precipitated, well-washed plumbic hydroxide (prepared by precipitating plumbic acetate with ammonium hydroxide) or with basic plumbic carbonate (prepared by precipitating plumbic acetate with sodium carbonate). When cool, filter, and decolorize the filtrate by warming it with animal charcoal. Evaporate to dryness on a water-bath. The residue, in addition to creatinine, contains creatine, which has resulted from the creatinine in the boiling with plumbic hydroxide. To separate them, treat the residue with cold concentrated alcohol, which will dissolve the creatinine and leave the creatine undissolved. Filter, and allow the filtrate to evaporate at ordinary temperature. Creatinine will separate in crystalline form.

SUGARS.

1. *Glucose group.* $C_6H_{12}O_6$.

Dextrose (polarizes light to the right).

Lactose.

Grape sugar.

Lævulose (polarizes light to the left).

Fruit sugar.

Mannitose.

Inosite.

Sorbine.

Etc.

Glucoses, by the action of a ferment, are converted into alcohol and carbon dioxide.



Diastase, a ferment, converts starch ($C_6H_{10}O_5$) into dextrose ($C_6H_{12}O_6$).

Starch warmed with dilute sulphuric acid or dilute hydrochloric acid is converted into dextrose (glucose).



Dextrine may be formed at the same time.



Dextrine is a gummy substance.

2. *Saccharose group.* $C_{12}H_{22}O_{11}$.

Saccharose (cane sugar).

Milk sugar.

Maltose.

Etc.

3. *Amylose group.* $C_6H_{10}O_5$.

Starch.

Dextrine.

Cellulose.

Arabinose.

Etc.

According to some investigators, the formula for starch, instead of $C_6H_{10}O_5$, should be $3C_6H_{10}O_5 = C_{18}H_{30}O_{15}$.

Other investigators suggest as the most probable formula $4C_6H_{10}O_5 = C_{24}H_{40}O_{20}$.

Starch is not estimated directly, but is converted into dextrose (glucose) by warming with dilute sulphuric acid or dilute hydrochloric acid. The quantity of starch is calculated from the quantity of dextrose (glucose) obtained.

ABNORMAL CONSTITUENTS OF URINE.

The substances occurring in the urine only pathologically, or only very seldom in soluble form, which need be considered are as follows:

Albumen; globulin; hemialbumose; peptone; mucin; glucose; milk sugar; inosite; dextrin; bile acids; bile coloring-matters; blood coloring-matter; uro-rubrohematin and uro-rubrofuscin; melanin; leucin; tyrosin; allantoin; fat, lecithin, and cholesterin; acetone and alcohol; Baumstark's substance, $C_5H_8N_2O_8$; urocaninic acid; sulphuretted hydrogen.

The abnormal constituents of the urine occurring most frequently, and of the greatest importance to the physician, are *glucose* and *albumen*.

DIABETIC URINE.

Urine containing glucose is diabetic urine.

Synonymes of glucose: dextrose, grape sugar, diabetic sugar.

Glucose is an abnormal constituent of urine.

It is not contained in normal urine, although Pavy claims that it is present in minute quantity in all urine.

Diabetic urine is generally paler in color than normal urine and has a sweet taste.

The quantity of urine voided in diabetes mellitus is usually greater than in health, and the urinous odor of normal urine is generally absent.

Its specific gravity, as a rule, is higher than that of normal urine (1030-1050, and even 1060).

Glucose may be present, varying from a trace up to 10-12 per cent., and even 14 per cent.

When diabetic urine is exposed to the air for a time, at not too low temperature, the surface often becomes covered with a scum or mould (fungus), due to the multiplication of cells of the *torula cerevisiæ*, originating from cells derived from the air.

A scum may also form on urine not containing glucose, but the scum in this case is not due to the *torula cerevisiæ*.

QUALITATIVE TESTS FOR GLUCOSE IN URINE.

1. *Moore's test*: To the urine contained in a test-tube add about one-fourth its volume of sodium or potassium hydroxide solution (about 10 per cent. strength) and boil. If glucose be present the liquid will become brown or black in color, depending upon the quantity of glucose.

Delicacy of the test, 0.3 per cent. glucose.

The test is unreliable, because normal constituents of the urine, particularly mucin, may give a similar coloration.

2. *Boettcher's test* (bismuth test): Add to the urine about one-fourth its volume of sodium or potassium hydroxide solution, or, better, a solution of sodium carbonate, and a portion of bismuth oxynitrate (subnitrate) about the size of a mustard-seed and boil.

If glucose be present the bismuth oxynitrate will be reduced to metallic bismuth, coloring the liquid first gray and then black, or the reduced metallic bismuth may settle in the bottom of the tube.

Delicacy of the test, 0.4 per cent. glucose.

Albumen interferes with this test by producing a similar change of color, due to the formation of black bismuth sulphide (Bi_2S_3). The albumen undergoes decomposition when heated with the caustic alkali, forming sodium sulphide (Na_2S) (the sulphur being derived from the albumen), which acts on the bismuth compound to form bismuth sulphide.

Albumen must be removed before employing this test.

3. *Johnson's picric acid test*: Picric acid (carbazonic acid, trinitrophenol), $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, is a derivative of carboic acid (phenol), $\text{C}_6\text{H}_5\text{OH}$.

Add to the urine a few drops of a saturated aqueous solution of picric acid and sufficient sodium hydroxide (NaOH), or KOH solution, to render it alkaline, and warm the liquid.

If glucose be present the liquid will become claret-red in color, owing to the production of picramic acid ($\text{C}_6\text{H}_2(\text{NO}_2)_2\text{NH}_2\text{OH}$), resulting from the replacement of one of the NO_2 radicals in picric acid by the NH_2 radical.

The picramic acid enters into combination with the alkali present to form a salt.

Delicacy of this test, 0.01 per cent. glucose.

This test is unreliable, because creatinine, a normal constituent of the urine, responds in a similar manner,—*i.e.*, gives a claret-red color.

4. *The fermentation test*: Depends upon the breaking up of glucose into alcohol and carbon dioxide by the action of a ferment,—*i.e.*, yeast.



Fill a test-tube with the urine, and add a few drops of brewer's yeast or a piece of compressed yeast about the size of a pea. Invert the tube over some of the same urine in a dish, and stand it aside for six or eight hours, keeping the temperature between 70° and 100° F.

If sugar be present it will undergo fermentation with the evolution of carbon dioxide, which will collect in the upper part of the inverted tube.

To prove that the gas in the tube is carbon dioxide, insert a piece of sodium hydroxide, close the opening of the tube with the thumb, and agitate the tube. The carbon dioxide will be absorbed by the sodium hydroxide, forming sodium carbonate.

As yeast itself may give off gas, a control experiment may be performed by testing the yeast in the same manner, but employing water in the test-tube in the place of urine.

Delicacy of the test, 0.4 per cent. glucose.

The quantity of carbon dioxide evolved from 0.4 per cent. of glucose is just sufficient, at ordinary temperature, to saturate the water in which it is contained, and therefore will not appear as gas in the upper part of the tube.

5. *Trommer's test*: Depends upon the reduction of cupric oxide (CuO) in alkaline solution by glucose to red cuprous oxide (Cu₂O) or yellow cuprous hydroxide (Cu₂(OH)₂).

Albumen must be removed from the urine before making Trommer's or Fehling's test.

To about 5 c.c. of the urine add about one-fourth its volume of sodium or potassium hydroxide solution. Then add, *drop by drop*, a solution of cupric sulphate (about 10 per cent. solution), and *agitate* the liquid until the bluish-white precipitate of cupric hydroxide (Cu(OH)₂) ceases to be dissolved and the liquid presents a slightly turbid or opaque appearance. Heat the liquid, and if glucose be present the cupric oxide will be reduced to red or brownish-red cuprous oxide or yellow cuprous hydroxide.

Delicacy of the test, 0.01 per cent. of glucose in the urine.

The cupric sulphate solution must never be added to urine containing sodium hydroxide while hot, or black cupric oxide will be produced.

Uric acid has the property of reducing cupric oxide in alkaline solution to cuprous oxide.

Creatinine has the property of reducing cupric oxide to cuprous oxide and redissolving the latter.

If on the addition of one drop of cupric sulphate solution to the urine rendered alkaline, and agitating the liquid, the bluish-white precipitate of cupric hydroxide is dissolved, the presence of glucose may be inferred.

Heat the liquid to the boiling-point, and if glucose be present, cuprous oxide should appear. The test, however, may fail to give visible cuprous oxide even though glucose be present.

In this case add several drops (3 to 6) of cupric sulphate solution to a fresh mixture of urine and sodium hydroxide, and agitate the liquid. If the bluish-white precipitate is dissolved, continue the addition of the cupric sulphate until the liquid presents a slightly turbid or opaque appearance. Heat the liquid, and if glucose be present a precipitate of cuprous oxide should appear.

If the bluish-white precipitate of cupric hydroxide produced from a few drops of cupric sulphate solution does not wholly dissolve, and heating fails to produce cuprous oxide, it may be concluded that glucose is not present. Its presence, however, is to be suspected when the specific gravity of the urine is high and the cupric hydroxide is dissolved.

If the cupric hydroxide is dissolved, and heating the liquid fails to give cuprous oxide, glucose may still be present, especially if the urine have a high specific gravity.

1. If more than 5 to 10 drops cupric sulphate solution are required to produce the turbidity, dilute a fresh portion of the urine with 4 or 9 volumes of water and apply Trommer's test (adding sodium hydroxide and 5 to 10 drops of cupric sulphate). If the cupric hydroxide wholly dissolves, and on heating unsatisfactory results are obtained, dilute a portion of the fresh urine more largely with water, and again apply the test.

2. If the results obtained by the foregoing methods are not satisfactory, as may be the case even when glucose is present

in large quantities, dilute Fehling's solution with about 4 volumes of water, heat to the boiling-point, and add to the hot liquid several drops of the suspected urine. The test may fail even when glucose is present, but the results are generally satisfactory.

3. If the results are still unsatisfactory, pass the urine through animal charcoal and test for glucose in the filtrate.

4. *Bruecke's lead process* for the removal of interfering substances.

If the results are unsatisfactory after having followed the foregoing directions, proceed with the lead process.

Lead process: Treat 50 c.c. of the urine with 60 c.c. of a 10 per cent. solution of commercial plumbic acetate, which precipitates the sulphates, phosphates, carbonates, coloring-matter, and some of the uric acid and creatinine. Filter, and wash the precipitate once or twice with water, and to the filtrate add excess of ammonium hydroxide, which precipitates the glucose in combination with lead as plumbic saccharate $(\text{PbO})_3(\text{C}_6\text{H}_{12}\text{O}_6)_2$.

Collect the precipitate on a filter and wash until free from ammonia. Suspend the precipitate in about 100 c.c. water, and pass a stream of hydrogen sulphide (H_2S) through the mixture until all of the lead is precipitated as black plumbic sulphide (PbS).

Filter, wash the precipitate once or twice, and evaporate the filtrate with wash-water to a volume of about 50 c.c., or until free from hydrogen sulphide.

After subjecting normal urine to the lead process and testing the final solution, a slight reduction of the cupric oxide may occur, due to the presence of a small quantity of uric acid which may have escaped removal in the process. This probably is the reason for the statement that glucose is a normal constituent of urine. Allow the final solution to stand twenty-four or forty-eight hours and the uric acid will separate in crystals, which may be filtered off and the tests for glucose applied to the filtrate, or evaporate the final solution to dryness on a water-bath, dissolve the glucose from the residue with alcohol, filter, evaporate the alcohol, and dissolve the residue in about 50 c.c. water, and apply the tests.

a. Apply Trommer's test to 5 or 6 c.c. of the liquid.

b. Apply Fehling's test to another portion.

About 50 per cent. of the glucose is lost in the course of the lead process.

6. *Fehling's test*: Depends upon the reduction of cupric oxide (CuO) in alkaline solution by glucose to red cuprous oxide (Cu_2O) or yellow cuprous hydroxide ($\text{Cu}_2(\text{OH})_2$).

Fehling's solution must *always* be tested before being used, by *diluting it with about four volumes of water* and heating to the boiling-point. If it has undergone decomposition, a reduction of the cupric oxide with the separation of cuprous oxide will occur on heating the diluted solution.

Fehling's solution which has undergone decomposition is unfit for use.

Application of Fehling's test: Dilute about 1 c.c. of Fehling's solution with about 4 c.c. of water and heat to the boiling-point, add the urine, 2 or 3 drops at a time, heating the liquid to the boiling-point after each addition of urine.

If glucose be present reduction will occur, and a precipitate of red cuprous oxide or yellow cuprous hydroxide will be formed.

Delicacy of the test, 0.001 per cent. glucose.

A considerable number of substances occur under normal or pathological conditions in the urine which possess the property of reducing cupric oxide in alkaline solution, such as uric acid, creatinine, creatine, allantoin, mucin, milk sugar, pyro-catechin, hydrochinon, bile coloring-matters, and glycosuric acid.

On the ingestion of certain compounds, such as benzoic acid, salicylic acid, glycerine, and chloral, substances appear in the urine which possess the property of reducing cupric oxide in alkaline solution.

7. *Test with phenylhydrazine hydrochloride* ($\text{C}_6\text{H}_5\text{N}_2\text{HCl} = \text{C}_6\text{H}_5\text{NHNH}_2\text{HCl}$) (Fischer's test, 1883): Depends upon the formation of a characteristic crystalline compound, phenyl-glukosazon, when phenylhydrazine hydrochloride is brought in contact with glucose. The compound usually separates in rosettes composed of yellow needle-shaped crystals, which melt at a temperature of 204° to 205°C .

Place in a test-tube twice as much phenylhydrazine hydrochloride as will cover the end of a penknife-blade, and into the same tube three times as much sodium acetate as will cover the end of a penknife-blade. Fill the test-tube about one-third with water, warm it slightly, and add an equal volume of the urine.

Stand the tube containing the mixture fifteen or twenty minutes in boiling hot water, and then in a vessel containing cold water.

If the urine contain a considerable quantity of glucose a yellow crystalline precipitate will appear almost immediately.

Sometimes the precipitate may appear amorphous macroscopically, and in such a case should be examined microscopically.

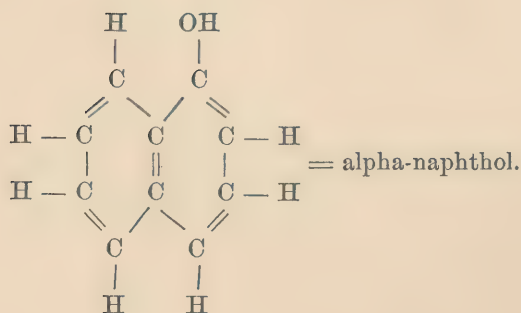
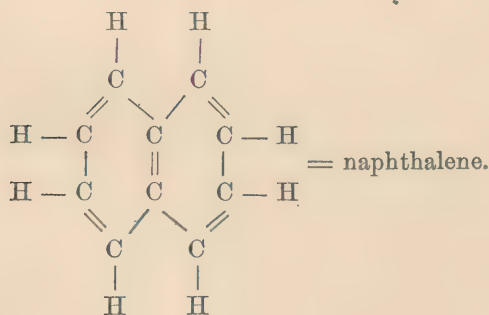
If the urine contains a small quantity of glucose, the liquid in the test-tube should be emptied into a conical glass and the sediment examined microscopically for yellow needle-shaped crystals. The occurrence of rather large yellow plates or brown globules does not indicate the presence of glucose.

Albumen does not interfere with this test, but if it be present in large quantity it is better to remove the greater part of it by boiling.

8. *Molisch's tests :*

a. *Test with alpha-naphthol* ($C_{10}H_7OH$).

Alpha-naphthol is a derivative of naphthalene.



Dilute the urine with water (about 100 of water to 1 of urine), and to 1 or 2 c.c. of the dilute urine add 2 drops of a 15 or 20 per cent. alcoholic alpha-naphthol solution. (The liquid may become turbid owing to the separation of some of the alpha-naphthol.) Add a volume of concentrated sulphuric acid equal to the volume of liquid in the test-tube, and if glucose be present a deep violet color, transitory in nature, will be produced. On diluting the liquid with water a bluish-violet precipitate will be formed.

Delicacy of the test, 0.00001 per cent. of glucose (1 part glucose in 10,000,000 parts water).

b. Test with thymol ($C_{10}H_{14}O = C_6H_3CH_3C_3H_7OH$, methyl-propylphenol).

The test is performed in a manner similar to the alpha-naphthol test.

Dilute the urine considerably with water (1-100), and to 1 or 2 c.c. of the liquid add 2 drops of a 15 or 20 per cent. alcoholic thymol solution. Add concentrated sulphuric acid equal in volume to the liquid in the test-tube. If glucose be present a deep cinnabar-red color will be produced, quickly changing to ruby-red, and then to carmine. On diluting with water the carmine color still remains.

Delicacy of the test, the same as the alpha-naphthol test.

Both of these tests fail to give a reaction with urea, uric acid, hippuric acid, creatinine, allantoin, pyro-catechin, and indican.

With cane sugar, fruit sugar, and maltose both these tests give reactions similar to those with glucose.

QUANTITATIVE ESTIMATION OF GLUCOSE IN URINE.

1. *Fermentation method*: Depends upon the fermentation of glucose in the urine, thereby causing a loss in the specific gravity of the urine, due to the formation of alcohol and the escape of carbon dioxide.



Theoretically, in fermentation, 180 parts glucose evolve 92 parts alcohol and 88 parts carbon dioxide. Then 1 part by weight of carbon dioxide lost is equivalent to the fermentation of 2.045 parts of glucose.

$$\begin{array}{cccc} CO_2. & C_6H_{12}O_6. & CO_2. & C_6H_{12}O_6. \\ 88 & : 180 & :: 1 & : 2.045 \end{array}$$

Method: Place 50 c.c. of urine in a small flask, and add a small portion of yeast. Close the flask with a perforated cork to which a small calcium chloride tube is attached (to collect moisture).

Weigh the entire apparatus, and stand it in a warm place that the glucose may ferment.

When the fermentation is completed, take the cork out of the bottle, and, by means of a glass tube, suck out the carbon dioxide which may occupy the air-space in the flask. Replace the cork, and weigh the entire apparatus. Each gramme lost is equivalent to 2.045 gm. glucose. To obtain the percentage, 50 c.c. of urine having been used, multiply the result by 2.

Water dissolves its own volume of carbon dioxide, therefore the 50 c.c. of liquid holds in solution 50 c.c. of carbon dioxide, which is weighed with the apparatus, and thus causes an error by adding excess of weight equal to the weight of carbon dioxide retained by the liquid.

To correct this error, add to the loss of weight the weight of 50 c.c. of carbon dioxide before multiplying by the factor 2.045.

1 c.c. CO_2 weighs 0.001971 gm.

$50 \times 0.001971 = 0.0985$ gm.

Example:

Weight of apparatus before fermentation, 67.6 gm.

“	“	“	after	“	65.6	“
					2.0	“ loss in weight.
					$\frac{0.0985}{2.0985}$	

+ weight of 50 c.c. $\text{CO}_2 = \frac{0.0985}{2.0985}$

$2.0985 \times 2.045 = 4.29$ gm. glucose in 50 c.c. urine; then to obtain the percentage (quantity in 100 c.c. urine),

$2 \times 4.29 = 8.58$ per cent. glucose.

Instead of the foregoing the correction may be made by adding the number 0.4 to the apparent percentage. 0.4 gm. glucose will evolve 0.1955 gm. CO_2 , or sufficient CO_2 to saturate 100 c.c. water.

	Glucose.		Carbon dioxide.		Glucose.		Carbon dioxide.
1.	180	:	88	::	0.4	:	0.1955 gm.

	CO_2 .		CO_2 .		CO_2 .		CO_2 .
2.	22320 c.c.	:	44 gm.	::	100 c.c.	:	0.1971 gm.

The 50 c.c. liquid absorbed 50 c.c. CO_2 , or 50×0.001971 gm. = 0.0985 gm. CO_2 , and as the calculation is made on the basis of 100 c.c. of liquid, $2 \times 0.0985 = 0.1971$ gm. CO_2 in 100 c.c. liquid, equivalent to 0.4 gm. glucose.

The first of the foregoing proportions shows that 0.1955 gm. CO_2 is evolved from 0.4 gm. glucose, and as 0.1971 gm. excess of weight of CO_2 is retained by 100 c.c. of liquid, the loss is compensated by adding the fixed number 0.4 to the apparent percentage.

Example:

Weight of apparatus before fermentation, 67.6 gm.

“	“	“	after	“	65.6	“
					2.0	“ loss in weight.

Then

$$2 \text{ gm.} \times 2.045 = 4.090 \text{ gm.} \times 2 = 8.18$$

$$\frac{0.4}{8.58} \text{ per cent. glucose.}$$

To obtain percentage in 100 parts of urine by weight.

Example:

Spec. grav. of urine.

1033	:	1000	::	8.58	:	X
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2. *Roberts's differential density method* for the estimation of glucose in urine: Depends upon the loss in specific gravity of the urine, due to the fermentation of glucose with the formation of alcohol, and evolution of carbon dioxide.

Each degree in specific gravity lost is equivalent to 1 grain of glucose in 437.5 grains (one imperial fluidounce) of urine.

Or referred to percentage by volume.

$$437.5 : 1 :: 100 : 0.23 \text{ per cent.}$$

Therefore one degree in specific gravity lost is equivalent to 0.23 per cent. of glucose.

Method: To 60 or 70 c.c. of urine add a small quantity of yeast, and put the liquid aside to ferment in a moderately warm place. As a control test take another portion of 60 or 70 c.c. of the same urine and stand it aside without the addition of yeast.

When the fermentation is completed take the specific

gravity separately of the fermented and unfermented urine. Deduct the specific gravity of the fermented urine from the specific gravity of the unfermented urine, and multiply the result by the factor 0.23. The result will be the percentage of glucose.

This method is the one most easily performed by the physician, and affords fairly accurate results.

3. *Fehling's method*: Depends upon the reduction of cupric oxide in alkaline solution by glucose to cuprous oxide.

Fehling's solution is prepared so that 1 c.c. of it shall equal 0.005 gm. glucose,—i.e., 0.005 gm. glucose will be required to reduce the cupric oxide in 1 c.c. of the solution to cuprous oxide.

Preparation of the solution: 5 molecules of crystallized cupric sulphate are reduced to cuprous oxide by 1 molecule of glucose.

Then

$C_6H_{12}O_6$.	$5CuSO_4 + 5H_2O$.	Glucose.	Cupric sulphate.
180	: 1247.5	:: 5 gm.	: 34.652 gm.

Therefore 34.652 gm. *cupric sulphate* will be reduced by 5 gm. *glucose*.

The cupric sulphate crystals, before being weighed, should be deprived of water held mechanically by being crushed and dried between bibulous paper.

1. Dissolve 34.652 gm. pure crystallized *cupric sulphate* in about 200 c.c. water.

2. Dissolve about 173 gm. *sodic potassium tartrate* ($KNaC_4H_4O_6$) (Rochelle salts) in about 480 c.c. of *sodium hydroxide solution* of 1.14 specific gravity. Slowly add the cupric sulphate solution to the Rochelle salts solution, stirring constantly.

The bluish-white precipitate of cupric hydroxide which appears will be completely dissolved by the liquid.

The object of the Rochelle salts is to hold the cupric hydroxide in solution.

Dilute the blue liquid with water to 1000 c.c., then

1000 c.c.	= 5.0	gm. glucose.
10 c.c.	= 0.050	" "
1 c.c.	= 0.005	" "

Fehling's solution may be prepared so as to avoid its undergoing decomposition by keeping the cupric sulphate and Rochelle salts solutions separately and mixing equal volumes of the two solutions when needed, viz.:

Dissolve the 34.652 grm. cupric sulphate in water and dilute to 500 c.c. Also dilute the Rochelle salts solution to 500 c.c., and keep the two solutions in separate bottles, closed with rubber stoppers.

To employ: mix 1 volume of the cupric sulphate solution with an equal volume of Rochelle salts solution.

Example:

5 c.c. cupric sulphate solution.	
5 c.c. Rochelle salts	"
10 c.c. Fehling's	"

The accuracy of the solution may be determined by titering it with a standard solution of glucose, prepared by dissolving 0.5 grm. glucose in 100 c.c. water.

The cupric oxide in 10 c.c. Fehling's solution should be exactly reduced by 10 c.c. of the glucose solution.

In using Fehling's solution the glucose solution must be added to the Fehling's solution, and not *vice versa*.

If the diabetic urine have a specific gravity of about 1035, dilute it with 4 volumes of water,—i.e., 10 c.c. of urine + 40 c.c. of water.

If the diabetic urine have a specific gravity of about 1040, dilute it with 9 volumes of water,—i.e., 10 c.c. of urine + 90 c.c. of water.

Albumen, if present in the urine, must previously be removed by coagulation and filtration.

Method: Place 10 c.c. of Fehling's solution (= 0.050 grm. glucose) in a beaker or dish and dilute with about 40 c.c. water. Heat to the boiling-point. Dilute the urine, if necessary, with 4 or 9 volumes of water, and run from 1 to 1.5 c.c. of the liquid from a burette into the hot diluted Fehling's solution. Apply heat to the Fehling's solution after each addition of urine to keep it at about the boiling-point. Continue the addition of the urine until the reduction of the cupric oxide is completed. This is recognized by the complete disappearance of the blue color of the liquid.

As the point of complete reduction is approached, the pre-

cupitate of cuprous oxide will subside more rapidly, thereby allowing the easy observance of the disappearance of the blue color of the liquid.

The first titration usually gives only approximate results unless performed with the greatest care. A second titration should be made, in which the urine (from 1 to 1.5 c.c. at a time) is run into the hot Fehling's solution until the quantity added is about 1 c.c. less than that employed in the first titration. Continue the addition of the urine, in small portions, until the blue color of the liquid is completely discharged.

Example: Suppose the urine employed had been diluted in the proportion of 1 volume urine to 9 volumes water, and 8 c.c. of this diluted urine had been required to reduce the cupric oxide in 10 c.c. Fehling's solution.

One-tenth of the 8 c.c. of liquid was urine, and must have contained 0.050 gm. glucose (the quantity of glucose required to reduce 10 c.c. Fehling's solution).

Then

Urine.	Glucose.	Urine.	Glucose.
0.8 c.c. :	0.050 gm.	::	100 c.c. : 6.25 per cent.

The estimation should be performed as rapidly as is consistent with accuracy.

If the urine mixture employed contain more than 0.5 per cent. glucose, it should be still further diluted with a measured volume of water.

If albumen be present, it must be removed before making the estimation.

CLINICAL APPLICATION OF FEHLING'S METHOD.

1 c.c. *Fehling's solution* = 0.005 gm. *glucose*.

a. Place 1 c.c. of Fehling's solution in a test-tube and dilute with 4 c.c. water (or use 5 c.c. of diluted Fehling's solution, consisting of 1 c.c. Fehling's solution and 4 c.c. water).

Heat to the boiling-point, add 1 c.c. of *undiluted* urine, and again heat the liquid.

If the blue color is entirely discharged, 0.5 per cent. or more glucose is present.

If the blue color is not entirely discharged, less than 0.5 per cent. glucose is present.

b. To 1 c.c. Fehling's solution + 4 c.c. water heated to the boiling-point add 0.1 c.c. of the same urine, and again heat the liquid.

If the blue color is entirely discharged, 5.0 per cent. or more glucose is present.

If the blue color is not entirely discharged, less than 5.0 per cent. glucose is present.

If the color is not discharged, add another 0.1 c.c. urine and again heat the liquid.

If the blue color is entirely discharged, 2.5 per cent. or more glucose is present.

If the blue color is not entirely discharged, less than 2.5 per cent. glucose is present.

Continue the addition of the urine 0.1 c.c. at a time and heating the liquid until the blue color is discharged.

Two drops of urine are approximately equal to 0.1 c.c.

Rule: Divide the number 5 by the number of tenths of urine employed, converted into whole numbers. The result will be the approximate percentage of glucose.

To obtain more accurate results, dilute the urine and titer in the usual manner with 10 c.c. Fehling's solution + 40 c.c. water.

Percentage amount of glucose present in urine, as indicated by the quantity of the urine required to exactly decolorize 1 c.c. of Fehling's standard solution diluted with water to 5 c.c.

Of UNDILUTED urine.

c.c. urine.	Glucose, per cent.	c.c. urine.	Glucose, per cent.
0.1 (5 ÷ 1)	5.0	0.4	1.25
0.12	4.2	0.45	1.10
0.14	3.5	0.5	1.0
0.16	3.1	0.6	0.83
0.18	2.7	0.7	0.71
0.2	2.5	0.8	0.62
0.25	2.0	0.9	0.55
0.3	1.66	1.0	0.5
0.35	1.4		

Of DILUTED urine (1 to 10).

c.c. urine.	Glucose, per cent.	c.c. urine.	Glucose, per cent.
0.4 (50 ÷ 4)	12.5	2.50	2.0
0.5	10.0	2.75	1.8
0.6	8.33	3.00	1.6
0.7	7.14	3.5	1.4
0.8	6.25	4.0	1.25
0.9	5.55	4.5	1.1
1.0	5.0	5.0	1.0
1.2	4.2	6.0	0.83
1.4	3.5	7.0	0.7
1.6	3.1	8.0	0.6
1.8	2.7	9.0	0.55
2.0	2.5	10.0	0.5
2.25	2.2		

4. *Estimating glucose by means of the saccharimeter:* If light which has undergone double refraction, as in passing through a crystal of Iceland spar, is examined with an analyzer, it is found that both the ordinary and extraordinary rays are completely polarized at right angles to each other. Advantage is taken of this in the construction of the saccharimeter or polariscope.

When 20.51 grm. anhydrous glucose are dissolved in water and diluted to 100 c.c., and an observation-tube 200 mm. in length filled with the solution is placed in Laurent's saccharimeter, the ray of light will be deflected to the right 100 markings or divisions, as indicated on the vernier-scale.

Hence 100 divisions on the scale = 20.51 grm. glucose.
1 division " " " = 0.2051 " "

Method: Mix 100 c.c. urine with 10 c.c. basic acetate of lead ($\text{Pb}_3\text{O}_2(\text{C}_2\text{H}_3\text{O}_2)_2$) solution, and filter through a dry filter. Fill the 200 mm. (standard) observation-tube with the filtrate.

The field of vision in the saccharimeter must be homogeneous in color, and the zero divisions on the vernier must correspond.

Place the observation-tube containing the urine in the saccharimeter, and note the effect on the field of vision. If the urine contain glucose, one-half of the field of vision will be darker than the other. Rotate the large thumb-screw until the field is again homogeneous in color.

Note the reading on the vernier. As the urine was diluted

one-tenth by the lead solution, the reading is one-tenth too low. This is corrected by adding one-tenth of the reading to the reading. Multiply the corrected reading by the value of each division on the vernier,—namely, 0.2051 grm.

Example :

$$\begin{array}{r} \text{Suppose the reading was } 23.1 \\ \text{Add } \frac{1}{10} \text{ to the reading, } \quad \underline{2.31} \\ 25.41 \end{array}$$

$$25.41 \times 0.2051 = 5.211 \text{ per cent. glucose.}$$

If the amount of glucose in the urine be very small, a 400 mm. observation-tube may be used. Then divide the corrected reading by 2 before multiplying by 0.2051.

RELATION OF SACCHAROSES AND AMYLOSES TO GLUCOSE.

	Mol. wt.	
Glucose, $C_{12}H_{24}O_{12}$ ($2C_6H_{12}O_6$),	= 360	= 100 glucose.
Saccharoses, $C_{12}H_{22}O_{11}$,	= 342	= 95 “
Amyloses, $C_{12}H_{20}O_{10}$ ($2C_6H_{10}O_5$),	= 324	= 90 “

SYNOPSIS OF ALBUMENS.

1. *Native albumens*, soluble in water.

- a. Serum albumen, not precipitated by ether.
- b. Egg albumen, precipitated by ether.
- c. Peptones.

2. *Globulins*, insoluble in water, but soluble in 1 per cent. solution of sodium chloride.

- a. Fibrinogen.
- b. Fibrinoplastin.
- c. Myosin.
- d. Vitellin.
- e. Crystallin.

3. *Derived albumens or albuminates*, insoluble in water or dilute sodium chloride solution, but soluble in acids or gastric juice.

- a. Acid albumen (syntonin).
- b. Alkali albumen.
- c. Casein.
- d. Fibrin.
- e. Coagulated albumen.
- f. Amyloid substance.

ALBUMEN IN URINE.

The albumen in urine in Bright's disease is serum albumen. Serum globulin in small quantity may also be present.

The quantity of albumen varies from a slight trace to 3 per cent.

Albuminous urine is usually pale in color and has a low specific gravity (1006 to 1014).

QUALITATIVE TESTS FOR ALBUMEN.

1. By heating the urine to the boiling-point.

a. If a flocculent precipitate appear, it is due either to earthy phosphates or coagulated albumen.

Treat the warm urine in which precipitation has occurred with one-tenth or one-twentieth its volume of nitric acid. If the precipitate be dissolved by the acid, it is composed of phosphates; if undissolved, it is albumen.

b. If no precipitate appear on boiling, treat the warm urine with one-tenth or one-twentieth its volume of nitric acid, and if albumen be present it will be precipitated. If the quantity of nitric acid be either too large or too small the precipitation of the albumen may not occur.

Serum albumen and globulin respond to this test. Peptone does not.

If the precipitate separates only after cooling, it is albumose.

2. Heller's method.

If not clear, the urine must be filtered before making the test.

Incline a test-tube, or better, a conical glass, containing strong nitric acid, and slowly pour the urine down the side so that it shall form a layer above the nitric acid. If albumen be present, a milky zone will be produced at the point of contact of the two liquids.

Delicacy of the test, 0.0025 per cent. albumen.

If the urine contain excess of urates a zone, due to the separation of uric acid, may be formed. This zone is brownish-red in color (the albumen zone is white), and forms, not at the point of contact of the urine and acid, but above. The under part of the zone is not so sharply defined as the albumen zone. If in doubt, dilute the urine nearly one-half with water and repeat the test. In this dilution uric acid will not interfere.

In the presence of albumen and excess of urates two zones will be produced,—the uric acid zone above the albumen.

On the administration of balsams—such as copaiba—a substance (abietic acid) appears in the urine which, with nitric acid, forms a zone similar to that formed by albumen. This substance also interferes with the first test, by separating as a flocculent precipitate on boiling the urine. The precipitate is soluble in alcohol, albumen is not.

If indican be present, the urine will become violet in color at the point of contact with the nitric acid. In presence of biliary matter it will become green, and then change to red-brown.

3. *Picric acid test* ($C_6H_2(NO_2)_3OH$) (carbazotic acid) (Galipe's test.)

Filter the urine if turbid.

a. Place a saturated aqueous solution of picric acid in a test-tube, and pour the urine down the tube above the picric acid solution (as in Heller's test). If albumen be present, a white zone will be produced.

b. Add the urine, drop by drop, to a saturated solution of picric acid, and, if albumen be present, a sharply defined turbidity will be produced at the point of contact of the drop of urine with the acid.

4. *Potassium ferrocyanide test.*

Filter the urine if not clear.

Strongly acidulate the urine with acetic acid (to 1 volume of urine add about $\frac{1}{4}$ volume of acid), and without heating add 3 or 4 drops of potassium ferrocyanide solution.

If albumen be present, a turbidity or a flocculent precipitate, depending upon the quantity of albumen, will be produced.

Delicacy of the test, 0.0025 per cent. albumen.

Serum albumen, globulin, and albumose respond to the test, but peptone does not.

5. *Biuret test for albumen*: Render the urine alkaline with sodium or potassium hydroxide, and add a few drops of dilute cupric sulphate solution. If albumen be present, the precipitate of cupric hydroxide will dissolve on shaking and a violet-red color will be imparted to the liquid.

Delicacy of test, 0.01 per cent.

Serum albumen, globulin, albumose, and peptone respond to this test.

QUANTITATIVE ESTIMATION OF ALBUMEN IN URINE.

1. *By weighing.*

Filter the urine if not clear.

Take 50 c.c. or 100 c.c. urine, depending upon the quantity of albumen present, warm to about blood-heat on a water-bath, and add acetic acid, drop by drop, until the albumen separates in flocculent masses. (The acetic acid keeps the earthy phosphates in solution). Heat the liquid to the boiling-point, and collect the coagulated albumen on an equipoised filter, wash with water until the filtrate fails to respond to the test for a chloride with argentic nitrate, or a drop of the filtrate fails to leave a residue when evaporated on platinum foil. Wash with alcohol, allow to dry at a temperature not above 100° C., and weigh.

The weight of albumen obtained is the quantity in the volume of urine employed.

2. *Esbach's method*: Depends upon the precipitation of albumen by picric acid.

The quantity of albumen is determined by measuring the height of the precipitate in a specially graduated tube, Esbach's albumenimeter.

The picric acid solution is prepared by dissolving 10 gm. picric acid and 20 gm. citric acid in 900 c.c. hot water, and, after cooling, diluting the solution to 1000 c.c.

Fill the albumenimeter-tube to the mark U with urine, and upon this pour the picric acid solution to the mark R. Close the opening of the tube with the thumb, and mix the liquids by inverting the tube several times.

Close the tube with a rubber stopper, stand it aside for twenty-four hours, and then read the height of the sediment on the scale.

The figures on the scale represent the number of grammes of albumen per 1000 c.c. urine.

The results are not absolutely accurate because of the precipitation of creatinine by picric acid, but sufficiently accurate for clinical purposes.

TOXICOLOGY.

A *poison* is any substance which, when taken into the body and either being *absorbed* or by its *direct chemical action* upon the parts with which in contact, or when applied *externally and entering the circulation*, is capable of producing deleterious effects.

CAUSES WHICH MODIFY THE EFFECTS OF POISONS.

a. Idiosyncrasy, or a peculiarity of constitution, may variously modify the effects of poisons.

b. Habit may render certain poisons harmless in doses which to most persons would prove rapidly fatal.

c. Disease.—In certain diseased conditions of the system there is a diminished susceptibility to the action of certain poisons, whilst in others there is an increased susceptibility, even to the action of the same substance.

d. Condition of the stomach: The presence of another substance or poison; sleep.

CLASSIFICATION OF POISONS.

a. Irritant poisons, as a class, produce irritation and inflammation of the stomach and bowels, attended or followed by intense pain in these parts, tenderness of the abdomen, and violent vomiting and purging, the matters evacuated being often tinged with blood.

The irritant poisons may be divided into three sections,—namely, mineral, vegetable, and animal.

b. Narcotic or cerebral poisons are such as act principally on the brain and spinal marrow, more especially on the former.

c. Narcotico-irritants partake, as indicated by their name, of the action of both the preceding classes.

SOURCES OF EVIDENCE OF POISONING.

1. *Evidence from symptoms.*

a. The symptoms occur suddenly, and soon after the taking of some solid or liquid.

b. The symptoms rapidly run their course.

2. *Evidence from post-mortem appearances.*

a. The *irritant* poisons, as a class, usually produce irritation and inflammation of one or more portions of the alimentary canal, the effects being sometimes confined to the stomach, while at other times they extend to a greater or less degree throughout the entire canal.

b. Narcotic poisons, in some instances, produce more or less distention of the veins of the brain, but in others they leave no marked morbid appearances, and in none are the appearances peculiar.

c. *Narcotico-irritants* partake, in the nature of their effects, of both the preceding classes.

APPEARANCES COMMON TO POISONING AND DISEASE.

a. *Redness* of the stomach and intestines as the effect of poisoning cannot in itself be distinguished from that arising from natural disease.

b. *Softening* of the stomach is another appearance which may give rise to embarrassment. When due to the action of poison, it is usually accompanied by other appearances which readily distinguish it from the effects of ordinary disease or post-mortem changes.

c. *Ulceration and perforation* of the stomach are not unfrequently produced by corrosive poisons, but they, especially the latter, are rarely met with as the result of the action of the simple irritants. As the effect of natural disease or post-mortem action they are not uncommon.

d. *Points to be observed in Post-mortem Examinations.*—All investigations of this kind should be made in the presence of the proper law officer; and it is well for the examiner to have the assistance and corroboration of another physician. All appearances observed, whether abnormal or otherwise, should be fully written down at the time of their observance.

All the organs and blood removed for the purpose of examination should be collected in *separate*, clean glass vessels, great care being taken that none of the reserved substances at any time be brought in contact with any substance that afterwards might give rise to suspicion. Before passing out of the sight of the examiner, the bottles should be securely sealed and fully labelled. They should then be retained in his sole possession until delivered to the proper person.

3. *Evidence from chemical analysis.*

a. In most charges of poisoning the final issue depends upon the results of the chemical analysis. In fact, in many instances in which the evidence from symptoms, post-mortem appearances, and moral circumstances is very equivocal or in part wanting a chemical examination may at once determine the true cause of death. It must be remembered, however, a person may die from the effects of poison and not a trace of its presence be discoverable in any part of the body; while, on the other hand, the mere discovery of a poison in the food or

drink taken, or in the body after death, is not in itself positive proof that it occasioned death.

b. Substances requiring Analysis.—The substances that may directly become the subject of a chemical analysis in a case of suspected poisoning are: the pure poison in its solid or liquid state; suspected articles of food or medicine; matters ejected from the body by vomiting or purging; the urine; suspected solids found in the stomach or intestines after death; the contents of the stomach or bowels; any of the soft organs of the body, as the liver, spleen, etc.; and the blood.

There are some poisons for which no definite chemical test is known.

Some poisons are detected by a combination of tests, and others by a single test or tests.

4. *Limit of tests.*

1 part of arsenic may be detected in 5,000,000 parts water.

Strychnine, $\frac{1}{100000}$ of a grain.

Hydrocyanic acid, $\frac{1}{100000}$ " " "

5. *Limit of recovery.*

6. *Failure to detect a poison.*

Numerous instances of poisoning are reported in which persons died from the effects of poison and none was discovered by chemical analysis in the body after death. This result has most frequently been observed in poisoning with organic substances, but it has happened when mineral poisons, and even those which are most easily detected by chemical tests, had been taken in large quantity.

A failure of this kind may be due to any of the following circumstances: 1. The poison may have been one of the organic poisons, which cannot at present be recognized by chemical tests. 2. The quantity present in the part examined may have been so minute as under the circumstances not to admit of recovery, or at least in a state sufficiently pure to permit its true nature to be established. 3. The poison may have been removed from the stomach and intestines by vomiting and purging or by absorption. 4. The absorbed poison may have been carried out of the system with the excretions. 5. If volatile, like hydrocyanic acid and some few other poisons, it may have been dissipated in the form of vapor. 6. It may have undergone a chemical change in the living body, or, especially if of organic origin, have decomposed in the dead body if far advanced in putrefaction.

7. *Caution regarding the purity of reagents.*

8. *Preservation of chemical results and material.*

9. *Duties and rights of experts.*

An expert cannot be compelled to make a post-mortem examination or chemical analysis.

Having made the examination, the knowledge acquired is common property.

The expert should be cautious in expressing opinions before the case is called for trial.

ARSENICUM. Atomic weight, 75.

In its pure state arsenicum has a steel-gray color, a bright metallic lustre, and has a crystalline structure. In dry air it remains unchanged, but in the presence of moisture it slowly absorbs oxygen and assumes a dark-gray appearance. It volatilizes at a temperature of 110°C . (230°F .).

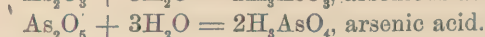
Metallic arsenic, when taken into the stomach, is capable of acting as a powerful poison, but perhaps only in so far as the metal becomes oxidized and converted into arsenious acid.

Compounds of arsenicum and oxygen:

As_2O_3 , arsenious oxide, molecular weight, 198.

As_2O_5 , arsenic " " " 230.

Both form acids with the elements of water:



Arsenious oxide (As_2O_3) is readily obtained by volatilizing metallic arsenicum in a free supply of air.

It is found in commerce either as a white or dull white, opaque powder, or in the form of large, hard masses.

Symptoms of Poisoning with As_2O_3 .—These are subject to great variation. Sooner or later after a large dose of the poison has been swallowed there is usually a sense of heat and constriction in the throat, with thirst, nausea, and burning pain in the stomach. The pain becomes excruciating, and is attended with violent vomiting and retching; the matters vomited present various appearances, being sometimes streaked with blood, and at other times of a bilious character; the pain in the stomach is increased by pressure. As the case progresses the pain extends throughout the ab-

domen, and there is generally severe purging and tenesmus; the matters passed from the bowels not unfrequently contain blood. The thirst usually becomes very intense; in some instances there is great difficulty in swallowing. The features are collapsed and expressive of great anxiety; the pulse is quick, small, and irregular; the eyes red; the tongue dry and furred; the skin cold and clammy, but sometimes hot; the respiration difficult; and sometimes there are violent cramps of the legs and arms. The urine is frequently diminished in quantity and its passage attended with great pain. Stupor, delirium, paralysis, and convulsions have also been observed. In many cases death takes place calmly, and the intellectual faculties remain clear to the last.

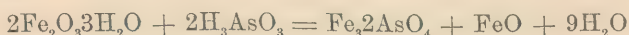
Fatal quantity: 2 grains taken in divided doses during a period of five days have proved fatal. On the other hand, 2 ounces have been ingested and recovery occurred in six hours.

When fatal: Usually in twelve to twenty-four hours, although in three cases death occurred in two hours, and in one case in twenty minutes.

Antidote: Hydrated ferric oxide (ferric hydroxide) is the most important chemical antidote.

The antidotal action of this substance is due to its forming an insoluble compound, ferric arsenate, with the arsenious oxide.

Thus,



The antidote should be given in its *moist* state and administered in large excess. The antidote has no action on arsenious oxide in its solid state, but only when in solution.

Hydrated ferric oxide (ferric hydroxide) may readily be prepared by treating ordinary tincture of ferric chloride with slight excess of ammonia, collecting the precipitate on a muslin strainer, and washing it with water until it no longer emits the odor of ammonia. A tablespoonful or more of the moist magma, mixed with a little water, may be given at a dose. The antidote should always be freshly prepared.

The ordinary magnesia of the shops may be used to add to the tincture of ferric chloride instead of ammonia, and the mixture containing excess of magnesia and hydrated ferric oxide may be administered at once without filtering.

Antiseptic Properties of Arsenic.—The preservative power of arsenic when brought in direct contact with animal textures is well known: and the poison seems to exert a similar action when carried by means of the circulation to the different tissues of the body. The bodies, therefore, of those who have died from the effects of this poison are not unfrequently found in a good state of preservation, even long periods after death.

Solid Arsenious Oxide. Tests.

a. It is volatile at a temperature of 138° C. (280° F.).

b. When heated on charcoal in the reducing flame it is dissipated in the form of white fumes, and emits a garlic-like odor.

c. When heated in a reduction-tube, arsenious oxide volatilizes without fusing, and recondenses in the cooler portion of the tube in the form of minute, octahedral crystals.

d. When heated in a reduction-tube containing a small piece of ignited charcoal, the arsenious oxide is volatilized and deoxidized in its passage over the ignited charcoal, and deposits in the cooler portion of the tube as a sublimate of metallic arsenic.

A similar reaction occurs when arsenious oxide is heated in a tube with a perfectly dry mixture of powdered charcoal and sodium carbonate.

If the closed end of the tube be removed (by breaking it off) and the metallic sublimate then heated, it is readily volatilized and oxidized into arsenious oxide, which condenses in octahedral crystals.

The metallic sublimate is soluble in a solution of either sodium or calcium hypochlorite.

e. When arsenious oxide is heated in a reduction-tube with a perfectly dry mixture of about equal parts sodium carbonate and potassium cyanide, reduction will take place and a sublimate of metallic arsenic will form in the cooler portion of the tube.

f. Potassium ferrocyanide may be employed as a reducing agent instead of potassium cyanide. The arsenious oxide is mixed with about 6 or 8 times its volume of dry potassium ferrocyanide, and heated in a tube as in the preceding test.

Solutions of Arsenious Oxide. Tests.

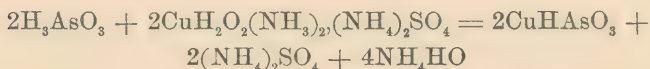
a. *Ammonio-silver nitrate test:* Ammonio-silver nitrate throws down from aqueous solutions of arsenious acid a bright-yellow

precipitate of tribasic silver arsenite (Ag_3AsO_3), the reaction being, perhaps,



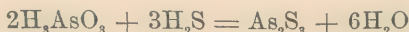
The precipitate is readily soluble, forming a colorless solution, in ammonium hydroxide and in nitric and acetic acids, sparingly soluble in ammonium nitrate, and insoluble in the fixed caustic alkalies.

b. Ammonio-copper sulphate test: Ammonio-copper sulphate produces in solutions of arsenious acid a green, amorphous precipitate of copper arsenite (CuHAsO_3), known also as Scheele's green, the reaction being, perhaps,



The precipitate is nearly insoluble even in large excess of the precipitant, but readily soluble in ammonia and in free acids. From very dilute solutions of the poison the precipitate does not appear of its characteristic color until the mixture has stood some time. The same precipitate is thrown down from solutions of neutral arsenites by copper sulphate alone.

c. Sulphuretted hydrogen test: Sulphuretted hydrogen throws down from solutions of arsenious acid, previously acidulated with hydrochloric acid, a bright yellow, amorphous precipitate of arsenious sulphide (As_2S_3), the reaction being



d. Reinsch's test: When a solution of free arsenious acid or an arsenite is strongly acidulated with hydrochloric acid, and the mixture boiled with a slip of bright metallic copper, the latter decomposes the arsenical compound and receives a coating of metallic arsenic, or an alloy of copper and arsenic (As_2Cu_5). The arsenical nature of the deposit may be shown in the following manner: the coated copper, after having been carefully washed with pure water and dried in a water-oven, is heated by means of a spirit lamp or the small flame of a Bunsen burner, in a narrow and perfectly dry and clean reduction-tube, when the arsenic volatilizes, and, becoming oxidized, yields a sublimate of octahedral crystals of arsenious oxide. This sublimate usually forms within from a quarter to half an inch above the point at which the heat is applied.

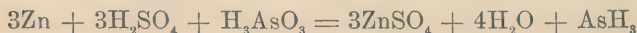
When the sublimate is not exceedingly minute, it presents a well-defined ring of sparkling crystals to the naked eye.

e. Marsh's test: When metallic zinc is treated with diluted sulphuric acid, the hydrogen of the latter is displaced by the metal with the formation of zinc sulphate, the hydrogen displaced passing off in its free state:



If, however, arsenious acid or arsenic acid, or any of the soluble compounds of the metal, be present, the nascent hydrogen decomposes the arsenical compound, and, uniting with the metal, forms arsenuretted hydrogen gas (AsH_3), which is evolved in its free state.

The reaction in the case of arsenious acid is as follows:



Metallic zinc is placed in the flask of the apparatus and a quantity of a cooled mixture of 1 volume of pure concentrated sulphuric acid and 4 volumes of distilled water, sufficient to cover the zinc, is poured in through a funnel tube and the decomposition of the acid allowed to proceed. If the zinc should act very slowly upon the acid, as is frequently the case with the pure metal, the action may be hastened by the addition of a few drops of platinic chloride.

Should the zinc or sulphuric acid be contaminated with arsenic this will give rise to arsenuretted hydrogen. Therefore, before applying the test to a suspected solution, the purity of the materials must be fully established. For this purpose, after the apparatus has become completely filled with hydrogen and while the gas is still being evolved, the outer uncontracted portion of the reduction-tube is heated to redness for about fifteen minutes or longer. If this fails to produce a metallic deposit or stain in the contracted part of the tube, in advance of the part heated, the material may be considered free from arsenic. The purity of the materials having been thus established, it may be necessary to wash and renew the zinc, dry the tubes, and add a fresh portion of the diluted acid.

The apparatus being adjusted and completely filled with evolved hydrogen, the jet of gas, as it issues from the drawn-out end of the reduction-tube, is ignited, care being taken not to apply a light until the whole of the atmospheric air is

expelled from the apparatus, as otherwise an explosion might occur. A small quantity of the arsenical solution is then introduced into the funnel-tube and washed into the flask by the subsequent addition of a few drops of the diluted sulphuric acid. The decomposition of the arsenical compound, with the evolution of arsenuretted hydrogen, will commence immediately. The presence of the arsenuretted gas may be established by three different methods,—namely,

- a. By the properties of the ignited jet.
- b. By decomposing it by heat applied to the reduction-tube.
- c. By its action upon a solution of argentic nitrate.

a. *The ignited jet:* As soon as the arsenical solution is introduced into the flask the evolution of gas increases. The flame of the jet will now increase in size, acquire a bluish tint, and, unless only a minute quantity of arsenic is present, evolve white fumes of arsenious oxide; so, also, the flame sometimes emits a peculiar garlic-like odor. If the white fumes be received upon a cold surface they condense to a white powder, which sometimes contains octahedral crystals. This is not a delicate method for detecting the presence of arsenic, and should never be employed to the exclusion of the following modification, viz.:

If the flame be allowed to strike against a cold body, as a piece of white porcelain, it yields a brown to black deposit of metallic arsenic.

Fallacy: Solutions of antimony, under these same conditions, undergo decomposition with the production of antimonuretted hydrogen, which, like arsenuretted hydrogen, burns with the evolution of white fumes, and yields metallic deposits upon cold surfaces applied to the flame. The spots produced by arsenic are readily soluble in a solution of either sodium or calcium hypochlorite, whereas those from antimony are insoluble, or dissolve only after prolonged digestion in the hypochlorite solution.

b. *Decomposition of the gas by heat:* When arsenuretted hydrogen, as evolved in Marsh's test, comes in contact with the red-hot portion of the reduction-tube, it is decomposed with the production of a deposit of metallic arsenic in the contracted part of the tube, in advance of the flame.

Fallacy: Antimonuretted hydrogen also is decomposed under

the above conditions with the deposition of metallic antimony. Antimony, however, is almost wholly deposited *before* reaching the part of the reduction-tube to which the flame is applied; when it yields deposits on both sides of the flame, the outer one is quite near the flame. On the other hand, arsenic deposits about one-half to three-quarters of an inch in advance, or on the *outer side* of the flame, and never before reaching the part of the tube to which the heat is directly applied.

c. Decomposition by argentic nitrate: If the reduction-tube of the apparatus be substituted by a tube bent at a right angle, and the arsenuretted hydrogen conducted into a solution of argentic nitrate, both the gas and the silver salt undergo decomposition with the production of arsenious acid, which remains in solution, and the separation of metallic silver, which falls as a black precipitate. The reaction is



The presence of arsenious acid in the solution may be shown by the usual tests for that substance.

SEPARATION OF ARSENIC FROM ORGANIC TISSUES.

Disintegrate the organic matter by means of hydrochloric acid and potassium chlorate, under the action of heat.

The following proportions of tissue, acid, and the chlorate yield very satisfactory results:

Treat 300 grm., or 10 ounces, of the solid tissue, as of the liver, cut into very small pieces and placed in a clean porcelain dish, with a mixture of 60 c.c., or 2 fluidounces, of strong hydrochloric acid and 240 c.c., or 8 fluidounces, of water.

Heat the mixture on a sand-bath, and when at about the boiling temperature, add about 1 grm., or 15 grains, of powdered potassium chlorate, and repeat the addition at intervals of a few minutes, with frequent stirring, until about 6 or 7 grm., or 100 grains, have been added and the mass has become homogeneous and of a light-yellow color. During this process water should occasionally be added to replace that lost by evaporation.

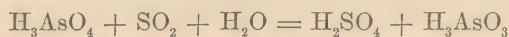
The disintegrating action of this mixture is chiefly due to the free chlorine and chlorine peroxide evolved by the mutual

decomposition of the chlorate and a portion of the hydrochloric acid.



Moderately heat the disintegrated mass until the odor of chlorine has entirely disappeared, and then allow to cool. Transfer the cooled mixture to a moistened linen strainer, and, when the liquid has all passed, wash the solids with a little warm water, the washings being collected separately. Concentrate the washings on a water-bath to a small volume, allow to cool, then add the washings to the first strained liquid, and filter the mixed liquid through paper. Any arsenic present will now exist as arsenic acid.

To the filtrate thus obtained add a solution of sulphurous acid until it smells strongly of the gas (sulphurous anhydride). Any arsenic acid present will be reduced to arsenious acid, in which form the metal is more rapidly and more completely precipitated by sulphuretted hydrogen than when it exists in the form of arsenic acid. The reducing action of the gas may be represented,



Concentrate the liquid on a water-bath to a volume twice that of the hydrochloric acid employed in preparing the mixture. Allow the concentrated liquid to cool, and then filter.

Pass a slow stream of washed sulphuretted hydrogen gas through the filtrate for several hours; then gently warm it, and allow to stand twelve to twenty-four hours. Any arsenic present will be precipitated as arsenious sulphide (As_2S_3), together with more or less organic matter and free sulphur. Should the liquid contain mercury, antimony, copper, or lead, these metals would also be precipitated as sulphides by the sulphuretted hydrogen. Liquids prepared as the above may yield with sulphuretted hydrogen a brownish or yellowish precipitate of organic matter and free sulphur, even in the absence of any metal.

Collect the precipitate on a small filter and wash, at first with water containing a little sulphuretted hydrogen, until the washings no longer contain chlorine (test with argentic nitrate).

Dissolve the moist precipitate on the filter with dilute ammonium hydroxide (1 to 10), which will dissolve any arsenious

sulphide present, with more or less of the organic matter and free sulphur. The sulphides of mercury, antimony, copper, and lead which might be present would remain undissolved, except perhaps a slight trace of the antimony sulphide.

Collect the ammoniacal liquid, usually of a dark-brown color, in a small porcelain dish and evaporate to dryness on a water-bath, treat the residue with a small quantity of strong nitric acid, and again evaporate the liquid to dryness; repeat the operation with nitric acid, if necessary, until the moist residue has a yellow color.

Moisten the residue with a few drops of concentrated solution of sodium hydroxide and evaporate to dryness. Treat the residue with several drops of concentrated sulphuric acid, and heat the mass on a sand-bath until it becomes about dry; again treat the residue with sulphuric acid and heat in the same manner until fumes of the acid are no longer evolved.

Pulverize, if necessary, the carbonaceous residue, and boil it with a small quantity of water containing a drop or two of sulphuric acid, cool the liquid, filter off, and wash the insoluble carbonaceous residue. If in the carbonization the whole of the free sulphuric acid was expelled, the resulting solution (filtrate) will be colorless and entirely free from organic matter. Concentrate the solution to a small and definite volume (say 20 c.c.), and divide it into two equal portions. Make the qualitative tests with one portion and the quantitative estimation with the other portion.

With the first portion

- a.* Apply Reinsch's test.
- b.* " Marsh's "

With the second portion of 10 c.c. make the quantitative estimation.

QUANTITATIVE ESTIMATION.

Acidulate the solution with a few drops of hydrochloric acid, warm to about blood-heat, and pass a stream of sulphuretted hydrogen through the liquid. The arsenic will be precipitated as arsenious sulphide. Collect the precipitate on an equipoised filter, wash at first with water containing a little sulphuretted hydrogen, then with pure water until the washings are free from chlorine. Dry the precipitate on the filter at a temperature of about 100 C., and weigh.

The quantity of As_2O_3 corresponding to the weight of As_2S_3 obtained is determined by

$$\begin{array}{c} \text{As}_2\text{S}_3. \\ 246 \end{array} : \begin{array}{c} \text{As}_2\text{O}_3. \\ 198 \end{array} :: \text{weight of precipitate} : X = \text{one-half,}$$

the amount of arsenic as As_2O_3 recovered from the quantity of organic tissue employed.

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